ABSTRACT

THE ELECTRONIC AND VIBRATIONAL SPECTRA OF THE μ -AMIDO-DECAMMINEDICOBALT(III) ION

by Arthur W. Chester

The electronic and vibrational spectra of the binuclear <u>µ</u>-amido-decamminedicobalt(III) ion were determined. The electronic spectrum was analyzed by means of the semiempirical molecular orbital method originated by Wolfsberg and Helmholz and improved by Ballhausen and Gray. The vibrational (infrared) spectrum was analyzed by means of normal coordinate analysis calculations.

The structure of the μ -amido-decamminedicobalt(III) ion has been determined by Vannerberg to be bent (C_{2v} symmetry) with a Co-N-Co bond angle of 144°. For the theoretical calculations a linear structure (D_{4h} symmetry) was assumed. The bond lengths were approximated from Vannerberg's data: the cobalt-amido nitrogen bond is 2.2 Å; the cobalt-equatorial ammine bond (perpendicular to the major axis) is 2.05 Å; the cobalt-axial ammine band (in the major axis) is 1.70 Å.

The molecular orbital calculations show that the two bands in the electronic spectrum with maxima at 19,740 and 28,010 cm.⁻¹ may be attributed to the electronic transitions $(d_{xz}, d_{yz}) \longrightarrow d_{x^2-y^2}$ and $(d_{xz}, d_{yz}) \longrightarrow d_{z^2}$ respectively on each cobalt atom. The ordering of the 3d orbital of the cobalt atoms is due to an axially compressed crystal field of C_{4v} symmetry. The very intense band with a maximum at 38,900 cm.⁻¹ is attributed to three L \longrightarrow M (reduction)charge transfer transitions.

Arthur W. Chester

Normal coordinate analysis calculations were performed separately for the two infrared regions (NaCl and CsBr). The ligand-vibrations in the NaCl region were similar to those observed in the hexamminecobalt(III) ion, except that three bands were observed in place of the one rocking vibration in the hexammine. The calculations indicated that these bands were due to the symmetric deformation vibrations of the axial and equatorial ammine groups (1305 and 1334 cm.⁻¹) and the NH₂ bending vibration (1378 cm.⁻¹). A very weak band at 1150 cm.⁻¹ is believed to be the NH₂ wagging vibration.

The frequencies and atomic motions of the skeletal vibrations of the μ -amido-decamminedicobalt(III) ion were calculated by use of force constants derived from the hexamminecobalt(III) ion. The calculated frequencies were correlated with the observed bands in the CsBr region. That similar force constants may be used for the different types of cobalt-nitrogen bonds indicates that the cobalt-amido bridge bond is electronically similar to simple cobalt-ammine bonds.

The electronic and infrared (NaCl region) spectra of a related ion, the μ -amido-chloroaquooctamminedicobalt(III) ion were also determined. The assymmetric band in the electronic spectrum with a maximum at 20,320 cm.⁻¹ was resolved into two bands of equal intensity. The resolved bands are attributed to the transition $(d_{xz}, d_{yz}) \longrightarrow d_{x^2-y^2}$ on each of the two cobalt atoms, which are now in different environments. A singlet-triplet transition was also found at 14,200 cm.⁻¹.

Arthur W. Chester

The relatively high intensity and the assignment of the band are discussed. The infrared spectrum of this compound is similar to that of the μ -amido-decamminedicobalt(III) ion and the assignments of the various ligand vibrational bands are discussed.

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Ву

Arthur W. Chester

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TABLE OF CONTENTS

| | Pa | ige |
|------|---|-----|
| I. | INTRODUCTION | 1 |
| II. | HISTORICAL | 7 |
| III. | THEORETICAL | 15 |
| | A. Molecular Orbital Theory for Transition Metal Ions | 15 |
| | B. Vibrational Analysis (Normal Coordinate Analysis) | 22 |
| | C. Electronic Spectra of Cobalt(III) Ammine Complexes | 27 |
| | D. Infrared Spectra of Cobalt(III) Ammine Complexes | 31 |
| IV. | EXPERIMENTAL | 33 |
| | Analytical Methods | 33 |
| | Preparation of Compounds | 34 |
| | Preparation of μ -amido-decamminedi- cobalt(III) Nitrate | 34 |
| | Preparation of μ -amido-decamminedi- cobalt(III) Chloride Dihydrate | 40 |
| | Stability of Solutions of the Bridged Complexes | 40 |
| | Preparation of Hexamminecobalt(III) Chloride | 40 |
| | Spectroscopic Measurements | 40 |
| ۷. | CALCULATIONS | 42 |
| | A. Molecular Orbital Calculations for the μ -amido-decamminedicobalt(III) Ion | 42 |
| | S tructure | 42 |
| | Bonding | 44 |
| | Radial Functions | 46 |

TABLE OF CONTENTS (Cont.)

VI

| | P | age |
|---------|---|------------|
| | Group Overlap Integrals | 46 |
| | Evaluation of the Atomic Overlap Integrals | 52 |
| | Valence State Ionization Energies | 5 3 |
| | Energy Calculations | 56 |
| в. | Vibrational Analysis Calculations | 59 |
| | The Cobalt-Ammine (Co-NH $_{3}$) Systems | 64 |
| | The Amido-Bridge System (Co-NH $_2$ -Co) | 67 |
| | The Hexamminecobalt(III) Ion | 67 |
| | The μ -amido-decamminedicobalt(III) Ion. | 69 |
| RESULT: | S AND DISCUSSION | 75 |
| Α. | Synthesis | 75 |
| в. | Electronic Spectra | 76 |
| с. | Molecular Orbital Calculations: Results and Discussion | 82 |
| | Results | 82 |
| | Bonding | 84 |
| | The Electronic Spectrum of the μ -amido- decamminedicobalt(III) Ion \ldots | 87 |
| | The Value of \underline{q} and the <u>SCCC</u> Treatment . | 92 |
| | The Spectrum of the Chloroaquo Ion \cdots . | 95 |
| D. | Infrared Spectra | 97 |
| | Infrared Spectra in the NaCl Region | 97 |
| | Far Infrared Spectrum of the μ -amido-decamminedicobalt(III) Ion \ldots | 103 |
| Ε. | Normal Coordinate Analysis Calculations: Results and Discussion | 103 |

•

TABLE OF CONTENTS (Cont.)

The Cobalt-Ammine and Amido Bridge
Systems105The Skeletal Vibrations of the µ-amido-
decamminedicobalt(III) Ion113REFERENCES.....123

Page

LIST OF TABLES

| TABLE | | PAGE |
|-------|--|------------------------|
| Ι. | Orbital transformation scheme for the μ -amido-decamminedicobalt(III) ion in D _{4h} symmetry | 47 |
| II. | Radial functions for the atomic orbitals used in the MO calculations | 48 |
| III. | Group overlap integrals for the μ -amido-decamminedicobalt(III) ion | 50 |
| IV. | The group overlap integrals for the μ -amido- decamminedicobalt(III) ion in terms of atomic overlap integrals | 51 |
| V. | Atomic overlap integrals | 5 3 |
| VI. | VSIE functions for cobalt | 55 |
| VII. | Coulomb energies used in the MO calculations | 58 |
| VIII. | Symmetry coordinates for the cobalt-ammine system (C _{3v} symmetry) | 66 |
| IX. | Symmetry coordinates for the amido-bridge system (C_{2v} symmetry) | 68 |
| х. | Symmetry coordinates for the μ -amido-decam-minedicobalt(III) ion (D _{4h} symmetry) | 72 |
| XI. | Electronic spectra of some bridged complexes | 77 |
| XII. | Parameters for the gaussian analysis of the electronic spectrum of $[(NH_3)_5CONH_2CoCl(NH_3)_5]$ $(NO_3)_5$ in water | 81 |
| XIII. | Parameters for the gaussian analysis of the electronic spectrum of $[H_2O(NH_3)_4CONH_2CoCl(NH_3)_4]$ Cl ₄ in 0.1 N HCl |) ₄] 81 |
| XIV. | Energy levels and molecular orbital coeffici- ents for the μ -amido-decamminedicobalt(III) is | on 83 |
| xv. | Infrared spectra of some bridged cobalt ammine complexes in the NaCl region | 99 |
| XVI. | Far infrared spectrum of μ -amido-decammine- dicobalt(III) nitrate \ldots | 104 |

LIST OF TABLES (Cont.)

| TABLE | | Page |
|--------|---|------|
| XVII. | Force constants for the cobalt-ammine systems | 106 |
| XVIII. | Force constants for the amido-bridged system | 106 |
| XIX. | Results of the normal coordinate analysis calculations for the cobalt-ammine systems | 107 |
| xx. | Results of the normal coordinate analysis calculations for the amido-bridge system . | 110 |
| XXI. | Force constants for the skeletal vibrations of the μ -amido-decamminedicobalt(III) ion. | 117 |
| XXII. | Results of the normal coordinate analysis calculations for the skeletal vibrations of the μ -amido-decamminedicobalt(III) ion | 118 |

.

LIST OF FIGURES

.

| FIGUR | E | Page |
|-------|--|-----------------------|
| 1. | The structure of the μ -amido-decamminedi- cobalt(III) ion | 5 |
| 2. | Qualitative ordering of the one-electron energy levels for tetragonal Co(III) complexes | 30 |
| 3. | The structure and molecular coordinate system of the μ -amido-decamminedicobalt(III) ion for the <u>MO</u> calculations | 43 |
| 4. | Structure and internal coordinates for the nor- mal coordinate analysis of the cobalt-ammine system | 65 |
| 5. | Structure and internal coordinates for the nor- mal coordinate analysis of the amido-bridge system | 65 |
| 6. | Structure and internal coordinates for the nor- mal coordinate analysis of the μ -amido-decammine- dicobalt(III) ion | - 71 |
| 7. | The electronic spectrum of μ -amido-decammine-dicobalt(III) nitrate in water | 79 |
| 8. | The electronic spectrum of the chloroaquo chloride in 0.1 N HCl \ldots | 80 |
| 9. | Proposed molecular orbital energy level diagram for the μ -amido-decamminedicobalt(III) ion | 85 |
| 10. | Dependence of coulomb energies of the various orbitals on the charge of the cobalt atoms | 93 |
| 11. | The infrared spectra of μ -amido-decamminedi-cobalt(III) chloride in the region 650-2000 cm. | ¹ 98 |
| 12. | The infrared spectum of $[H_2O(NH_3)_4CoNH_2CoCl(NH_3)]$ $Cl_4 \cdot 4H_2O$ in the region 650-2000 cm. | 4 []] 102 |
| 13. | Schematic diagrams of the A_{2u} and E_{u} skeletal vibrations of the μ -amido-decamminedicobalt(III) ion | 120 |

I. INTRODUCTION

The phenomenon of a bridging group joining two metal ions occurs widely in the chemistry of transition metal ions. The group which occurs most frequently as a bridge between metal ions is the hydroxyl group. The phenomenon of OH bridge formation is known as "olation"¹. Other groups, however, also act as bridges; the amido (NH_2^-) , nitro (NO_2^-) , sulfato (SO_4^{2-}) , and peroxo (O_2^{2-}) groups are some representative examples. Most of the metals in the first transition series form bridged, polynuclear complexes. The most extensively investigated polynuclear complexes have been those of chromium and cobalt.

The hexacoordinated complexes of trivalent cobalt played a central role in the development of modern coordination chemistry by A.Werner and have continued in this role up to the present. In the course of his investigations, Werner prepared most of the polynuclear cobalt complexes known today. Werner was able to demonstrate conclusively the octahedral structure of cobalt(III) complexes when he resolved one of these compounds, the tris $(di-\mu-hydroxo$ tetramminecobalt(III)) cobalt (III) ion, $[Co{(HO)_2Co(NH_3)_4}_3]^{6+}$ into its optical antipodes³. It was the first completely inorganic compound to be so resolved.

In more recent times, bridging groups have played an important role in the study of the kinetics of electron transfer reactions. Taube^{4,5} and Halpern^{6,7} have shown that

the group \underline{X} in the reaction

 $Co(NH_3)_5X^{2+} + Cr^{2+} + 5H^+ = Co^{2+} + CrX^{2+} + 5NH_4^+$ can facilitate electron transfer by formation of a bridge between the cobalt and chromium ions. The formation of bridged intermediates has been shown to be important in other electron-transfer reactions, e.g. the U(IV)-U(VI) exchange and the U(IV)-Tl(III) reaction⁸. Halpern and Orgel⁹ and Libby¹⁰ have proposed mechanisms for these reactions. Since there has been much interest in this laboratory in electron transfer reactions involving bridged intermediates^{11,12}, an investigation of stable bridged complexes seemed in order.

Among the most interesting stable bridged complexes are the so-called " μ -peroxo" complexes of cobalt. These compounds were first properly characterized by Werner², who proposed the currently accepted formulae. Two members of the " μ -peroxo" series are the μ -peroxo-decamminedicobalt (III,IV) ([(NH₃)₅COO₂CO(NH₃)₅]⁵⁺), and μ -peroxo- μ -amidooctamminedicobalt(III,IV) ([(NH₃)₄CO(NH₂,O₂)CO(NH₃)₄]⁴⁺) ions. These compounds are paramagnetic and contain what are formally trivalent and quadrivalent cobalt atoms. Since quadrivalent cobalt is not known in any other compound, the stability exhibited by these compounds seems unusual. However, electron paramagnetic resonance studies of some of these compounds have demonstrated that the two cobalt atoms are equivalent^{13,14} thus invalidating the cobalt(IV) assignment. Recently, Schaefer and Marsh¹⁵ have shown by

a single-crystal X-ray diffraction study that the oxygenoxygen distance is more typical of a superoxide ion. This determination agrees with the proposal of Gleu and Rehm¹⁶ that the paramagnetism is due to the superoxide ion rather than to the cobalt atoms.

The relationship of the peroxo complexes to synthetic reversible oxygen carriers is also of interest. Synthetic oxygen carriers are usually cobalt(II) complexes of Schiff bases or amino-acids which reversibly absorb and release molecular oxygen¹⁷. Synthetic oxygen carriers are also formed from other transition metal ions, such as iron(II), nickel(II) and copper(II), but the largest number are derived from cobalt(II). These compounds are of importance as model compounds for the study of oxygenation mechanisms in natural oxygen carriers such as the hemoglobins and hemocyanins.

The oxygenation-deoxygenation process may be illustrated by the cobalt(II)-histidine system¹⁸:

 $CoL_2 + O_2 = [CoL_2]_2O_2$ (L = histidine)

From the formulation of the oxygenated complex, it seems probable that it is a binuclear complex containing an oxygen bridge between the cobalt atoms. Other oxygen carriers are similar. The valence states of the cobalt atoms and the oxygen bridge are not known. It seems probable that these compounds are structurally similar to the μ -peroxo-decamminedicobalt(III,IV) ion (which can be considered as an irreversible oxygen carrier) and thus fall into the realm of bridged complexes.

It was initially intended that this investigation be concerned with a theoretical study of the oxygen bridge in the peroxo complexes of cobalt. However, it was found that there was a notable lack of knowledge regarding the electronic structures of "normal" bridged complexes (those which exhibit normal metal ion oxidation states) and the differences between the "normal" complexes and the μ -peroxo complexes would be unclear. Such a view was reinforced by the lack of certain knowledge (at the time) of the structures of the peroxo complexes. It was felt, then, that there would be more to gain initially with a theoretical investigation of a model bridged compound containing normal valence states as well as a simple bridging group.

The compound chosen for this study was the μ -amido-decamminedicobalt(III) ion:

 $[(NH_3)_5 CONH_2 CO(NH_3)_5]^{5+}$.

This compound is the simplest member of the series of binuclear ammine complexes of cobalt(III) and corresponds to the octahedral hexamminecobalt(III) ion of the mononuclear cobalt(III) ammine series. This complex was first prepared and thoroughly characterized by Werner^{2,19} in 1908. More recently, the structure of the nitrate salt of this ion was determined by Vannerberg²⁰ by X-ray diffraction techniques. The structure is shown in Figure 1. The unit cell is tetragonal with

> a = 11.68 ± 0.03 Å c = 8.28 ± 0.02 Å.



Figure 1. The structure of the μ -amido-decamminedicobalt ion²⁰. Open circles are NH₃ groups, dark circles are cobalt atoms, hatched circle is the NH₂ group. (The four NH₃ groups perpendicular to the plane are not shown.) Since the molecule is bent, it has C_{2v} symmetry.

For the theoretical investigation of the electronic and vibrational spectra of this molecule, the simplifying assumption was made that the bridge is linear, i.e. the cobalt-nitrogen-cobalt angle is 180° instead of the reported 144° . This approximation has a relatively small effect on calculated electronic energy levels, but has a somewhat larger influence on vibrational frequencies. These effects will be discussed in the body of the thesis.

II. HISTORICAL

Polynuclear complexes of cobalt were prepared as long ago as 1852. At that time, $\operatorname{Fremy}^{21}$ prepared the diamagnetic <u>µ</u>-peroxodecamminedicobalt(III) ion by oxidation of an aqueous ammonical cobalt(II) solution. Work in the next few decades centered on the preparation of the diamagnetic and paramagnetic <u>µ</u>-peroxodicobalt salts²²⁻²⁷. In the course of those investigations, other bridged products were isolated from the oxidized solutions. The products were generally mixtures from which other <u>µ</u>-peroxodicobalt complexes could be prepared. The most important of the products were the "Melanochlorid"²²⁻²⁴, from which various complexes containing three bridges can be obtained, and the "Fuskosulfat" (now known as Vortmann's Sulfate)^{21,24,25,27}, from which complexes with one or two bridges can be obtained.

It was not until the first decade of the 20th century that the nature of these polynuclear complexes was fully understood. At this time Werner published a series of ten papers in which he unambiguously demonstrated the formulae and chemical properties of the above mentioned products as well as many new polynuclear cobalt(III) complexes^{2,19,28-35}.

Werner gave complete preparations for both the "Melanochlorid"² and Vortmann's Sulfate³³ as well as determining the nature of major constituents of each. He reported the preparation and structural formulae of salts of such ions as di- μ -hydroxo-octamminedicobalt(III)³², tri- μ -hydroxohexamminedicobalt(III)³⁴, μ -amido- μ -hydroxo-octamminedicobalt(III)^{3,3}

 μ -sulfato- μ -amido-octamminedicobalt(III)² and the μ -amidodecamminedicobalt(III)^{2,19}. In addition, he prepared and characterized other triply-bridged, binuclear cobalt complexes containing bridging groups such as peroxo, hydroxo, nitro, amido, and acetato² as well as complexes in which the ammine groups in some of the above ions were replaced by ethylenediamine groups². In the last paper of the series², Werner gave a coherent, if somewhat lengthy, summary of the results which led to his proposed structures.

With the exception of the $\underline{\mu}$ -peroxodicobalt compounds, relatively few reports concerning bridged complexes have appeared in the literature since Werner's last paper concerning them. Werner³ reported the successful resolution of the "hexol" ion $[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$ and of the $\underline{\mu}$ peroxo- $\underline{\mu}$ -amido-tetrakis(ethylenediamine)dicobalt(III,IV) ion^{3.6}. Meyer, Dirska, and Clemens³⁷ reported the preparation of the selenate salts of some bridged complexes, as well as complexes in which a selenate group acts as the bridge.

Very little work has been reported regarding the spectra of "normal" bridged complexes. The first report is that of Shibata³⁸ in 1916 on the visible and ultraviolet spectrum of the μ -amido- μ -hydroxo-octamminedicobalt(III) ion. He reported a band at 21,000 cm.⁻¹ and one at 34,000 cm.⁻¹. Due to his rather primitive equipment, however, these values give only a qualitative representation of the spectrum. The next report is that of Ohyagi³⁹. He determined the

visible and ultra-violet spectra of phosphoric acid solutions of most of the polynuclear cobalt ammine complexes originally prepared by Werner. The spectra were rather crude and are indicative only of the relative band positions and the number of bands. The fact that Ohyagi's spectra do not agree with the positions of the maxima and, in some cases, the line shapes reported in the present and other investigations, is undoubtedly due to the primativeness of his equipment (colorimetric). Inamura and Kondo⁴⁰ have also reported the spectra of a number of hydroxo-bridged cobalt ammine complexes.

More recently, in connection with other investigations, the positions of maxima and molar absorptivities of some bridged cobalt complexes have been reported⁴¹⁻⁴³. The visible and ultra-violet spectra of the paramagnetic <u>u</u>peroxo-decamminedicobalt(III,IV) ion have been more extensively investigated^{39,44-46}.

Reports of the infrared spectra of the polynuclear cobalt ammines are even more scarce. Blyholder and Ford⁴⁷ have reported the far infrared (CsBr region) spectra of a number of dihydroxo-bridged cobalt ammines. They have assigned a strong band at 530 cm.⁻¹ to the motion of the cobalt-oxygen four membered ring and a band at about 500 cm.⁻¹ to the cobalt-nitrogen stretching vibration. Vannerberg and Brosset⁴⁸ have reported the infrared spectrum of μ -peroxo-decamminedicobalt(III,IV) nitrate in the rock-salt region. They found peaks at 3200 cm.⁻¹ (N-H stretching),

1630 cm.⁻¹, 1350 cm.⁻¹, and a double peak with maxima at 820 and 840 cm.⁻¹.

Since Werner's work^{2,19,28-35}, little has been reported until recently on the reactions of bridged cobalt ammine complexes. Charles and Barnartt⁴⁵ studied the products of the decomposition of the diamagnetic salt μ peroxo-decamminedicobalt(III) sulfate in aqueous sulfuric acid. They identified four of the products of the decomposition as Co^{2+} , $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_5H_2O]^{3+}$ and $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$ and proposed a mechanism to account for their formation. Sykes has investigated the oxidationreduction reactions of the μ -peroxo- μ -amido-octamminedicobalt(III, IV) ion with Fe^{2+49} and of the μ -peroxo-decamminedicobalt(III,IV) ion with Fe^{2+} , SO_3^{-} , NO_2^{-} , $S_2O_3^{-}$, V(IV)and Sn(II)^{50,51} and with iodide ion⁵². Reisel has investigated the role of some bridged cobalt ammines, including the μ -peroxo complexes, in the catalytic decomposition of hydrogen peroxide^{52a}.

More recently, Mast and Sykes^{42,43} have studied the interconversion reactions of binuclear cobalt ammines. They reported both chemical and kinetic evidence for the existence of the diaquo complex $[H_2O(NH_3)_4CONH_2CO(NH_3)_4OH_2]^{5+}$ a complex not previously prepared. They also studied the kinetics of some intramolecular substitution reactions in doubly-bridged complexes⁴³. Garbett and Gillard have reported some interconversion^sof similar complexes with ethylenediamine ligands⁴¹ and have assigned optical configurations to these complexes⁵³.

The structures of three bridged cobalt ammines have been investigated by single crystal X-ray diffraction techniques. Vannerberg and Brosset determined the crystal structure of the nitrate of the μ -peroxo-decamminedicobalt (III, IV) ion⁴⁸. Their determination, based on 234 reflections and a final R factor of 0.19, indicated that the O_2 group lies perpendicular to the Co-Co axis and that the oxygen-oxygen distance is 1.45 Å. Schaefer and Marsh¹⁵, however, have determined the structure of the sulfate tris(bisulfate) salt of this ion based on 1458 reflections and a final R factor of 0.077. They found that the oxygen bridge structure was very similar to that of hydrogen peroxide, i.e. not perpendicular to the cobalt-cobalt axis. Each cobalt atom is surrounded by an almost perfect octahedron of 5 nitrogen atoms and one oxygen atom. Moreover, they found the oxygen-oxygen distance to be 1.31 Å, a distance more typical of superoxide than peroxide ion⁵⁴. Their cobalt-cobalt distance, 4.56 Å, compared well with that of Vannerberg and Brosset (4.52 \AA) .

Vannerberg also investigated the structure of di- μ hydroxo-octamminedicobalt(III) chloride tetrahydrate⁵⁵ and μ -amido-decamminedicobalt(III) nitrate²⁰. The structure of the μ -dihydroxo complex may be described as two octahedra sharing one edge, as expected. The cobaltoxygen bond length is 1.94 Å and the cobalt-oxygen-cobalt angle is 110°. The two cobalt atoms and two oxygen atoms lie in a plane which also contains two ammine groups on each cobalt atom. The Co-Co distance is 2.97 Å and the oxygen-oxygen distance is 2.49 Å. The structure of the μ -amido-decamminedicobalt(III) ion was mentioned previously (Introduction) and is shown in Figure 1. From the data given by Vannerberg, a cobalt-cobalt distance of 4.18 Å is calculated.

Theoretical calculations and discussions of bridged cobalt ammine complexes have been confined to the μ -peroxodicobalt compounds. Dunitz and $Orgel^{56}$ assumed the O_2 bridge to be linear $(D_{4h}$ molecular symmetry) and calculated the approximate ordering of the molecular orbitals by group-theoretic techniques. They concluded that the unpaired electron occupies an antibonding orbital composed of oxygen 2p orbitals and that the formulation of this ion should then be $[(NH_3)_5Co^{3+}(O_2^{-})Co^{3+}(NH_3)_5]^{5+}$, i.e. the bridge is a superoxide ion. The ordering of higher lying antibonding orbitals was not determined in this qualitative treatment and spectral transitions can not be assigned. Since the assumption of a linear bridge is a good approximation to the structure recently determined by Schaefer and Marsh¹⁵, more importance will have to be accorded this treatment in the future.

Vlĉek⁵⁷ assumed the oxygen bridge to be perpendicular to the Co-Co axis (D_{2h} molecular symmetry) and applied group theoretic techniques to the system. He concluded that the unpaired electron occupies a molecular orbital involving both oxygen (p_y) and cobalt (d_{yz}) orbitals. He

obtained similar results with the μ -peroxo- μ -amido-dicobalt system. Vannerberg and Brosset later found a structure similar to Vlĉek's assumed structure⁴⁸, but Schaefer and Marsh's recent improvement¹⁵ tends to invalidate Vlĉek's treatment.

Ebsworth and Weil have also discussed the electronic structure of the peroxo complexes based on electron paramagnetic resonance spectra¹⁴. They concluded that the unpaired electron in the paramagnetic peroxo complexes occupies an antibonding π -orbital extending over both cobalt atoms and the oxygen bridge. Weil and Goodman⁵⁸ studied the electron paramagnetic resonance spectrum of μ -peroxo- μ -amido-tetrakis(ethylenediamine)dicobalt(III,IV) nitrate in a matrix of µ-amido-µ-nitro-tetrakis(ethylenediamine)dicobalt(III) nitrate. They concluded from the high g values that the unpaired spin arises from a hole in an otherwise filled molecular orbital and, from the extent of anisotropy in the g values, that this hole is centered primarily on the cobalt atoms. It will be necessary to reinterpret the e.p.r. results in the light of the structure determined by Schaefer and Marsh¹⁵.

Goodman, Hecht and Weil have adequately reviewed earlier theoretical work on the peroxo complexes⁵⁹.

There has been no reported theoretical work on the "normal" bridged cobalt ammines. However, other bridged systems have been treated qualitatively. Dunitz and Orgel⁵⁶ treated the μ -oxodecachlorodiruthenate(IV) ion group-

theoretically. Jezowska-Trzebiatowska and Wojciechowski⁶⁰ have also discussed the molecular orbital theory of a number of oxo-bridged complexes.

Two reviews concerning the theory and chemistry of the peroxodicobalt complexes are available in the recent literature^{59,61}. The preparation and properties of all the known polynuclear cobalt ammines are thoroughly summarized in "Gmelins Handbuch der anorganischen Chemie"⁶².

III. THEORETICAL

A. Molecular Orbital Theory for Transition Metal Ions

Molecular orbital theory was first applied to transition metal complexes by Wolfsberg and Helmholz⁶³, who treated the tetrahedral oxyanions MnO_4^- , CrO_4^- and $ClO_4^$ semiempirically. The Wolfsberg-Helmholz treatment was later improved by Ballhausen and Gray⁶⁴ in their treatment of tetragonal vanadyl complexes. Molecular orbital (<u>MO</u>) theory was then applied to a variety of complexes⁶⁵⁻⁷¹. The subject has been discussed in a number of recent books⁷²⁻⁷⁴ and some of the methods of calculation employed have been illustrated^{64,70,72,74}.

The Wolfsberg-Helmholz treatment is essentially that of the Linear Combination of Atomic Orbitals-Molecular Orbital (<u>LCAO-MO</u>) method⁷⁵. In general, the molecular orbitals are taken as linear combinations of the atomic orbitals of the atoms in the molecule. In the case of transition metal complexes, the bonding and antibonding molecular orbitals (<u>MO</u>'s) are generally given by:

$$\Phi^{b}(MO) = c_{1}\psi_{1} + c_{2}\psi_{2} \qquad (3A-1a)$$

$$\Phi^{\bullet}(MO) = c_{1}'\psi_{1} + c_{2}'\psi_{2} \qquad (3A-1b)$$

where the primes indicate antibonding orbitals and $\underline{\psi_1}$ and $\underline{\psi_2}$ refer to the metal and ligand basis functions (in general the subscript 1 refers to the metal, 2 refers to the ligands). The functions $\underline{\psi_1}$ and $\underline{\psi_2}$ are linear combinations of the simple atomic orbitals ϕ_{1j} and ϕ_{2j} :

$$\psi_{1} = \Sigma a_{i} \phi_{1i} \qquad (3A-2a)$$

$$\psi_{2} = \Sigma b_{i} \phi_{2i} \qquad (3A-2b)$$

In some cases, hybrid orbitals can be used for metal or ligand orbitals. The hybrid orbitals can be written in the form⁶⁴

 ψ (hybrid) = (sin θ) ϕ (s) ± (cos θ) ϕ (p or d) (3A-3)

The coefficients of the <u>MO</u>'s are normalized according to the equations:

$$c_1^2 + c_2^2 + 2c_1c_2G_{12} = 1$$
 (3A-4)
 $c_1^2 + c_2^2 + 2c_1c_2G_{12} = 1$

Here G_{12} is the group overlap integral

$$G_{12} = \int \psi_1^* \psi_2 \, d\tau$$
 (3A-5)

which can generally be evaluated in terms of simple atomic overlap integrals $(S_{ij})^{76}$.

The approximate energy of orbitals such as (1a) or (1b) can be obtained by application of the Variation Method^{75,77}. The energy, E, is given by

$$\mathbf{E} = \int \Phi^* \, \widehat{\mathbf{H}} \Phi d\tau / \int \Phi^* \Phi d\tau \qquad (3A-6)$$

where $\underline{\hat{H}}$ is the one-electron Hamiltonian operator. Expanding (6) using the bonding orbital (1a) and the following definitions:

$$H_{ij} = \int \psi_i^* \hat{H} \psi_j d\tau \qquad (3A-7a)$$

$$G_{ij} = \int \psi_i \psi_j \, d\tau \qquad (3A-7b)$$

and assuming that $\underline{\psi_1}$ and $\underline{\psi_2}$ are normalized, \underline{E} can then be written:

$$E = \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 + c_2^2 + 2c_1 c_2 G_{12}}$$
(3A-8)

Since <u>E</u> must be stationary with respect to $\underline{c_1}$ and $\underline{c_2}^{78}$, we can write the conditions $\frac{\partial E}{\partial \underline{c_1}} = 0$ and $\frac{\partial E}{\partial \underline{c_2}} = 0$. Application of these conditions result in the <u>Secular Equations</u> for <u>E</u>:

$$c_{1}(H_{11}-E) + c_{2}(H_{12}-EG_{12}) = 0$$

$$c_{1}(H_{12}-EG_{12}) + c_{2}(H_{22}-E) = 0$$
(3A-9)

In the general case of <u>N</u> orbitals forming the <u>MO</u>, <u>N</u> linear equations of the following form result from a similar set of conditions $\left(\frac{\partial E}{\partial c_i} = 0\right)$:

$$\sum_{i=1}^{n} (H_{ij} - EG_{ij})c_{i} = 0 (j = 1, 2, ..., n)$$
(3A-10)

In order to obtain non-trivial solutions $(c_i \neq 0)$ of (10) it is necessary that the determinant of the coefficients of the c_i be zero:

$$H_{ij} - EG_{ij} = 0 \qquad (3A-11)$$

The linear equations (10) may be expressed as a matrix secular equation:

$$\underline{H} \underline{C} = \underline{G} \underline{C} \underline{E}$$
(3A-11a)

Here, all matrices have their rows and columns labeled by the basis orbitals.

<u>H</u> = the Hamiltonian matrix, with the elements given by (7a).
 <u>G</u> = the overlap matrix, with the elements given by (7b).
 <u>E</u> = the diagonal eigenvalue matrix, the elements being the energies of the MO's.

 \underline{C} = the eigenvector matrix, the elements being the coefficients c_i of the <u>MO</u>'s.

To solve the secular determinant (11) for the values of <u>E</u>, it is necessary to obtain the values of the $\underline{H}_{\underline{i}\underline{i}}$ (coulomb integrals), $\underline{H}_{\underline{i}\underline{j}}$ (resonance integrals) and the $\underline{G}_{\underline{i}\underline{j}}$. The coulomb integrals are usually evaluated as <u>Valence State</u> <u>Ionization Energies</u> (<u>VSIE</u>). The <u>VSIE</u>'s are sensitive to the charge and electronic configuration of the ion. Values of the <u>VSIE</u> are obtained from tables of atomic spectra⁷⁹ and have been tabulated by Ballhausen and Gray^{74} .

The value of $\underline{H}_{\underline{ij}}$ was originally approximated by Wolfsberg and Helmholz⁶³ as:

$$H_{ij} = F_{x} G_{ij} \frac{H_{ii} + H_{jj}}{2} \qquad (3A-12)$$

where the <u>x</u> refers to <u>o</u> or <u>m</u> orbitals. Values of $\underline{F}_{\underline{\sigma}} = 1.6$ and $\underline{F}_{\underline{\pi}} = 1.87$ were used. Ballhausen and Gray improved the Wolfsberg-Helmholz approximation by calculating H_{ij} as the geometric mean⁶⁴:

$$H_{ij} = FG_{ij} \sqrt{H_{ii} H_{jj}} \qquad (3A-13)$$

The geometric mean is preferable, because the resonance energy is expected to decrease rapidly as the difference in the coulomb energies becomes greater. Ballhausen and Gray used a value of 2.0 for \underline{F} in equation (13) in their treatment of the vanadyl ion⁶⁴.

The secular determinant (11) can be conveniently factored by the use of group theory in the case of symmetric molecules^{72,82}. Thus, to obtain the values of \underline{E} , it is usually necessary to solve several determinants of low order (2 or 3) rather than one of order \underline{N} (the number of orbitals considered.) The coefficients c_1 and c_2 for each <u>MO</u> can then be obtained for each value of \underline{E} by use of the normalization conditions (4) and the linear equations (10).

The coefficients $\underline{c_i}$ in each <u>MO</u> are then used for electronic population analysis⁸³. The population of each orbital \underline{i} is computed from the normalization condition

$$\Sigma c_{i}^{2} + 2\Sigma c_{i}c_{j} G_{ij} = 0 \qquad (3A-14)$$

where $\underline{c_i}^2$ represents the net population of orbital \underline{i} and the term $\underline{2\Sigma} \ \underline{c_i} \ \underline{c_j} \ \underline{G_{ij}}$ represents the "<u>overlap population</u>". The final population of each type of atomic orbital (e.g. 3d, 4s, or 4p) is computed by assuming that the overlap population is evenly divided. The fraction of charge residing in the \underline{i}^{th} orbital of the \underline{n}^{th} <u>MO</u> is given by:

$$POP(ni) = c_{ni}^{2} + \sum_{i \neq j} c_{ni} c_{nj} G_{ij} \qquad (3A-15)$$

The configuration and charge of each atom can be computed by summing the <u>POP(ni)</u> for each type of atomic orbital. These new values of the charge and configuration may then be used to compute new <u>VSIE</u> and the <u>MO</u> calculation can be recycled until the input and output charges and configuration converge. This recycling is known as the Self-Consistent Charge-Configuration (<u>SCCC</u>) method⁸¹.

Fenske has published a critique of the <u>MO</u> method as applied to complexes in a study of the octahedral TiF_6^{3-} ion⁸⁴.

Bedon, Horner and Tyree⁷⁰ had made the original calculations for TiF_6^{3-} . Their calculated energy levels indicated excellent agreement with the experimental value of 10Dg (the energy difference between the metal d_{xy} , d_{xz} , d_{yz} (t_{2q}) and d_{z^2} , $d_{x^2-v^2}$ (e_g) orbitals in an octahedral ligand field). Fenske studied the effect on the calculated energy levels of a) varying the hybridization of the ligand orbitals, b) the inclusion of ligand-ligand overlap, c) the inclusion of low-lying energy levels, and d) the influence of the ligand VSIE. His results showed that the calculated energy difference 10Dq was affected greatly by small variations in the input data. For instance, the inclusion of the very small effect of ligand-ligand overlap changed the calculated value of 10Dq by 2300 cm.⁻¹. Also, the calculated value was almost doubled by ignoring ligand orbital hybridization, even though it had been shown in at least one case that unhybridized orbitals result in better agreement with experimental data⁶⁸. Fenske concluded that the semiempirical Wolfsberg-Helmholz MO treatment described above should be accepted only with strong reservations and that continued theoretical investigations will be necessary to eliminate the uncertainties inherent in it.

Recently, the effect of varying the value of \underline{F} in equation (12) has been studied for octahedral^{80,81} and tetrahedral⁸¹ complexes. Cotton and Haas found that no single value of \underline{F} gave consistently good results for octahedral ammine complexes of the first transition series and that

variation of \underline{F} was necessary to fit experimental spectral data⁸⁰. Basch, Viste and Gray found that the best value of \underline{F} for octahedral complexes of metals of the first transition series with halogen or oxygen ligand could be represented by

 $F_{\sigma}(n) = [0.027n + 1.546] \pm 0.02$ (3A-16)

where $\underline{n} = 0$ for Ti, $\underline{n} = 1$ for V, etc. regardless of the oxidation state involved⁸¹.

The Wolfsberg-Helmholz <u>MO</u> method has been principally applied to the interpretation of the electronic spectra of complexes^{63-68,70-72,80,81} and has been useful in the interpretation of electron paramagnetic resonance spectra⁸⁵. It is possible also to predict the polarization of spectral transitions from <u>MO</u> energy level diagrams by the use of group theory^{72,82}. This application of group theory can be a powerful tool in assigning transitions if polarization data are available.

Fenske has shown that quantitative agreement between calculated and observed transition energies is to be considered fortuitous⁸⁴. The Wolfsberg-Helmholz <u>MO</u> method involves many severe approximations, some of which have already been mentioned. Other approximations used will be discussed below in the description of the calculations.

The results of <u>MO</u> calculations by the Wolfsberg-Helmholz method will indicate, at best, only the relative ordering of the energy levels in a given complex and may make possible the assignment of the observed electronic transitions. The results of the calculations on the μ -amidodecamminedicobalt(III) ion (and, indeed, on any other complex ion) should be regarded as only a qualitative ordering of energy levels.

B. Vibrational Analysis (Normal Coordinate Analysis)

Infrared absorption spectra of molecules have been of great importance to chemists for the understanding of molecular structure and properties. In general, molecular vibrations are the cause of the absorption of infrared radiation by molecules. The spectrum of a molecule in the infrared region can then be called its vibrational spectrum and the theoretical analysis of the spectrum is known as vibrational analysis. The method used to analyze the vibrational spectrum of polyatomic molecules is known as <u>Normal Coordinate Analysis</u>. The principles of normal coordinate analysis have been set forth in detail by a number of authors⁸⁶⁻⁹⁰.

The vibrational motions of a molecule may be described by displacements along the <u>3N</u> axes of the molecule (where <u>N</u> is the number of atoms), e.g. along the x, y, and z axes of each atom. Since the kinetic energy, <u>T</u>, of a particle of mass <u>M</u> and velocity <u>V</u> is given by <u>T</u> = $1/2 \text{ MV}^2$, the total kinetic energy of a molecule is given by

$$2T = \sum_{j=1}^{3N} m_{i} \dot{x}_{i}^{2} \qquad (3B-1)$$

where $\underline{\mathbf{m}}_{\underline{\mathbf{i}}}$ is the mass associated with the displacement coordinate $\underline{\mathbf{x}}_{\underline{\mathbf{i}}}$ and $\underline{\mathbf{\dot{x}}}_{\underline{\mathbf{i}}}$ is the time derivative of $\underline{\mathbf{x}}_{\underline{\mathbf{i}}}$:

$$\dot{x}_i = dx_i/dt$$
 (3B-1a)

In treating molecular vibrations, it is more convenient to speak of internal coordinates, such as bond stretching or angle deformation coordinates. The internal coordinates $\frac{R_k}{k}$ may be expressed as linear combinations of the cartesian displacement coordinates x_i :

$$R_{k} = \sum_{i=1}^{3N} B_{ki} \times (k = 1, 2, ..., 3N - 6)$$
 (3B-2)

The sum over <u>k</u> runs to $3\underline{N} - 6$ because it can be shown⁸⁸⁻⁹⁰ that any molecule will have $3\underline{N} - 6$ unique vibrations when translational and rotational movements are disregarded. Equation (2) may be expressed in matrix notation as:

$$\underline{\mathbf{R}} = \underline{\mathbf{B}} \underline{\mathbf{X}} \tag{3B-2a}$$

where \underline{R} and \underline{X} are the column matrices of the internal coordinates and cartesian displacement coordinates, respectively.

By defining a set of quantities G_{kl} as

$$G_{kl} = \sum_{i=1}^{3N} B_{ki} B_{li} / m_i$$
 (k, l = 1,2,...,3N - 6),(3B-3)

it has been shown⁸⁶ that the kinetic energy of the molecule can be expressed in terms of the internal coordinate velocities $\frac{\dot{R}_{ki}}{ki}$ as

$$2T = \underline{\dot{R}}' \underline{G}^{-1} \underline{\dot{R}}$$
 (3B-4)

where $\underline{\underline{G}}^{-1}$ is the inverse of the matrix $\underline{\underline{G}}$, which has the elements given in equation (3); $\underline{\underline{R}}$ is the column matrix of the

internal coordinate velocities and $\underline{\dot{R}}$ ' is its transpose (in general, the matrix \underline{A} ' is the transpose of \underline{A}).

It can also be shown⁸⁸ that the potential energy, \underline{V} , may be expressed in a similar fashion:

$$2V = \underline{R}' \underline{F} \underline{R} \qquad (3B-5)$$

where \underline{F} is the matrix of the force constants connecting the internal coordinates R_k .

The normal coordinates Q_k (k = 1, 2, ..., 3N) are defined as linear combinations of the mass-weighted Cartesian coordinates $\underline{q_i} = \underline{m_i} \times \underline{x_i}$ as:

$$Q_{i} = \sum_{i=1}^{3N} l_{ji} q_{j} \quad (j = 1, 2, ..., 3N) \quad (3B-6)$$

such that the kinetic and potential energies have the form:

$$2T = \sum_{i=1}^{3N} \dot{Q}_{i}^{2} \qquad 2V = \sum_{i=1}^{3N} \lambda_{i} Q_{i}^{2} \qquad (3B-7)$$

where the λ_i are constants, i.e. the potential energy has no cross terms. If the equations (7) are combined with LaGrange equations of motion, given by:

$$d/dt(\partial T/\partial q_i) + \partial V/\partial q_i = 0$$
 (i = 1,2,...,3N) (3B-8)

then the equations of motion of the system are given by

$$\dot{Q}_{i} + \lambda_{i} Q_{i} = 0 \qquad (3B-9)$$

Equation (9) has the solutions:

$$Q_{i} = Q_{i}^{0} \sin(\sqrt{\lambda_{i}} t + \delta_{i}) \qquad (3B-9a)$$

where $\underline{Q_{i}^{0}}$ and $\underline{\delta_{i}}$ are the amplitude and phase constants respectively, and $\underline{Q_{i}}$ is normal coordinate position at time \underline{t} . The frequency $\underline{v_{i}}$ of the $\underline{i}^{\text{th}}$ normal vibration is related to $\underline{\lambda_{i}}$ by

$$v_{i} = (1/2\pi c)\sqrt{\lambda}_{i} \text{ cm.}^{-1} \qquad (3B-9b)$$

Normal coordinate analysis finds the frequencies of vibration, $\underline{v_i}$, and the normal coordinates $\underline{Q_i}$ associated with these frequencies by the use of matrix algebra. The trans-formation \underline{L} , defined by

$$\underline{\mathbf{R}} = \underline{\mathbf{L}} \ \underline{\mathbf{Q}} \ \text{or} \ \underline{\mathbf{Q}} = \underline{\mathbf{L}}^{-1} \ \underline{\mathbf{R}} \tag{3B-10}$$

is sought such that the kinetic and potential energy matrices given by equations (4) and (5) are diagonalized:

$$2T = \underline{\dot{R}}' \underline{G}^{-1} \underline{\dot{R}} = \underline{\dot{Q}}' \underline{L}' \underline{G}^{-1} \underline{L} \underline{\dot{Q}} = \underline{\dot{Q}}' \underline{E} \underline{\dot{Q}} \qquad (3B-11a)$$

$$2V = \underline{R}' \underline{F} \underline{R} = \underline{Q}' \underline{L}' \underline{F} \underline{L} \underline{Q} = \underline{Q} \underline{\Lambda} \underline{Q}$$
(3B-11b)

In (11a) and (11b), $\underline{\underline{E}}$ is the unit matrix and $\underline{\underline{A}}$ is a diagonal matrix with the elements $\underline{\underline{\Lambda}}_{\underline{1}\underline{i}} = \underline{\lambda}_{\underline{i}}$. From (11a) and (11b), it can be seen that

<u>L' F L</u> = <u>A</u> and <u>L' G⁻¹ L</u> = <u>E</u> (3B-12) Solving for <u>L</u>' in the second equation in (12) (<u>L'</u> = <u>L</u>⁻¹ <u>G</u>) and substituting the result in the first equation, the vibrational secular equation is obtained:

$$\underline{G} \underline{F} \underline{L} = \underline{L} \underline{A}$$
(3B-13)

The values of the $\frac{\lambda_i}{\lambda_i}$ can then be obtained by solving the secular determinant:

$$\left|\underline{G} \ \underline{F} \ - \ \underline{E}\lambda_{i}\right| = 0 \tag{3B-14}$$

From the values of $\underline{\lambda_i}$, the transformation matrix $\underline{\underline{L}}$ (or $\underline{\underline{\underline{L}}}^{-1}$) from equation (10) may be determined. The rows of the matrix $\underline{\underline{\underline{L}}}^{-1}$ give the normal coordinate $\underline{Q_i}$ in terms of an unnormalized linear combination of the internal coordinates R_k .
The secular determinant (14) may be considerably simplified by the introduction of the symmetry properties of the molecule. The internal coordinates, \underline{R}_k , can be transformed into symmetry coordinates, \underline{S}_k , by use of an orthogonal matrix \underline{U} :

$$\underline{S} = \underline{UR} \tag{3B-15}$$

Equations (10) are then replaced by:

$$\underline{S} = \underline{U} \underline{L} \underline{Q} = \underline{L}_{S} \underline{Q}$$
(3B-16)
$$\underline{Q} = \underline{L}^{-1} \underline{U}^{-1} \underline{U} \underline{R} = \underline{L}_{S}^{-1} \underline{S}$$

where

$$\underline{\mathbf{L}}_{\mathbf{S}} = \underline{\mathbf{U}} \ \underline{\mathbf{L}} \tag{3B-16a}$$

The \underline{G} and \underline{F} matrices may then be "<u>symmetrized</u>", or reduced to block diagonal form, by use of the orthogonal transformations

$$\underline{G} = \underline{U} \underline{G} \underline{U}' \qquad (3B-17a)$$

$$\underline{\mathbf{F}}_{\mathbf{S}} = \underline{\mathbf{U}} \ \underline{\mathbf{F}} \ \underline{\mathbf{U}}' \tag{3B-17b}$$

(since $\underline{\underline{U}} = \underline{\underline{\underline{U}}}^{-1}$ for an orthogonal matrix). The vibrational secular equation (13) then becomes

$$\underline{G}_{S} \underline{F}_{S} \underline{L}_{S} = \underline{L}_{S} \underline{A} \qquad (3B-18)$$

and the secular determinant (14) is then

$$\left|\underline{G}_{s} \underline{F}_{s} - \underline{E}\lambda_{i}\right| = 0 . \qquad (3B-19)$$

If the proper \underline{U} matrix has been used, the secular determinant (19) will be in block diagonal form, resulting in considerable simplification in finding the solutions λ_i .

C. Electronic Spectra of Cobalt(III) Ammine Complexes

The electronic spectra of cobalt(III) ammine complexes have been examined by many workers (for instance, Linhard and Weigel^{91,92}), and have been treated theoretically by both crystal field theory^{93,97} and molecular orbital theory 80,93,98,99. The spectra of Co(III) ammines are generally characterized by two weakly to moderately intense bands ($\leq \leq 10^2$) in the visible and near-ultraviolet spectral regions which may be characterized as d \rightarrow d transitions on the basis of their intensities.

Crystal field theory (<u>CFT</u>), in which the ligands act only as point charges or point dipoles, has been applied more successfully than <u>MO</u> theory. The parent member of the cobalt(III) ammine series is the octahedral hexamminecobalt(III) ion. Substituted Co(III) ammines are considered to have the basic octahedral structures with relatively small tetragonal or trigonal perturbations, so that the spectra may be qualitatively understood with reference to an octahedral structure.

According to <u>CFT</u>, the five degenerate <u>d</u> orbitals are split under the influence of an octahedral field into a lower t_{2g} (d_{xy} , d_{xz} , d_{yz}) and an upper e_g ($d_{x^2-y^2}$ and d_{z^2}) level.

The ground state of the Co(III) ion in a strong octahedral crystal field is t_{2g}^6 , a closed shell configuration of symmetry ${}^{1}A_{1g}$. The first excited state results from the

promotion of an electron from the t_{2g} level to the e_g level, giving a configuration of $t_{2g}^5 e_g$. The configuration $t_{2g}^5 e_g$ gives rise to two triply-degenerate singlet states, ${}^{1}T_{1g}$ and ${}^{1}T_{2g}$ and two triplet states, ${}^{3}T_{1g}$ and ${}^{3}T_{2g}$. The energy separation of the ${}^{1}T_{1g}$ and the ${}^{1}T_{2g}$ states is due to correlative interactions between the electrons, whose roles have been subordinated by the crystal forces⁹⁶. The two bands observed may then be assigned to the transitions ${}^{1}A_{1g}$ $\rightarrow {}^{1}T_{1g}$ and ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$, and the energies of these transitions are given by

$$E(^{1}T_{1g}) - E(^{1}A_{1g}) = -35 F_{4} + 10Dq$$

$$E(^{2}T_{1q}) - E(^{1}A_{1q}) = 16 F_{2} - 115 F_{4} + 10Dq$$

where $\underline{F_2}$ and $\underline{F_4}$ are the Condon-Shortley interelectronic repulsion integrals¹⁰⁰ and 10Dq is the energy separation between the t_{2q} and e_q levels.

Transitions from the ground state to the triplet levels ${}^{3}T_{1g}$ and ${}^{3}T_{2g}$ have been observed 92,101 in the near-infrared region. Since these transitions are spin-forbidden, their intensities are very low ($\leq \leq 1$), although surprisingly high intensities have been found for some bromo- and iodo-sub-stituted Co(III) ammines 92 . The energies of the two singlet \rightarrow triplet bands are given by

$$E({}^{3}T_{1g}) - E({}^{1}A_{1g}) = -105F_{4} + 10Dq$$

 $E({}^{3}T_{2g}) - E({}^{1}A_{1g}) = 8F_{2} - 24F_{4} + 10Dq.$

When the symmetry of the octahedral Co(III) ammine complexes is lowered by substitution of other ligands, the degenerate t_{2g} and e_g levels are split to give lower orbital degeneracies. Of particular interest are complexes of tetragonal symmetry such as the halopentammines (C_{4v}) or the <u>trans</u>-dihalotetrammines (D_{4h}). If the notation of the point group C_{4v} is used for either case, the t_{2g} level splits into a doubly degenerate e level (d_{xz} and d_{yz}) and a non-degenerate b_2 level (d_{xy}), and the e_g level splits into two non-degenerate levels, $a_1(d_{z2})$ and $b_1(d_{x2-y2})$.

The qualitative ordering of these one-electron levels in the case of axial elongation is shown according to the predictions of \underline{CFT} in Figure 2(a) and according to the predictions of MO theory in Figure 2(b). The two theories differ in the ordering of the e and b, levels, in that \underline{MO} theory takes metal-ligand $\underline{\pi}$ -bonding into account. Figure 2(c) shows the qualitative ordering of the one-electron levels in the case of axial compression predicted by MO or CFT. The ground state of tetragonal Co(III) complexes in any of the three cases shown in Figure 2 is e^4 b_2^2 . The promotion of electrons from the filled e and b, levels to the unfilled a_1 and b_1 levels results in the observed spectra⁹⁷. Many tetragonal cobalt(III) complexes exhibit splitting of the band corresponding to the ${}^{1}A_{1} \longrightarrow {}^{1}T_{1q}$ band of the octahedral hexammine and it is predicted on the basis of diagrams such as Figure 2 that the ${}^{1}A_{1q} \longrightarrow {}^{1}T_{2q}$ band should also be split, although this phenomenon has not yet been

| $b_1 \equiv d_{x^2-y^2}$ | ^b 1 | ^a 1 |
|--|----------------|----------------|
| $a_1 \equiv d_{z^2}$ | a <u>1</u> | ^b 1 |
| $b_2 \equiv d_{xy}$ | e | e |
| $\frac{e \equiv d_{xz}, d_{yz}}{xz, yz}$ | ^b 2 | ^b 2 |
| (a) | (b) | (c) |



- (a) <u>CFT</u> prediction for axial elongation (without $\underline{\pi}$ -bonding)
- (b) <u>MO</u> theory predictions for axial elongation (with $\underline{\pi}$ -bonding)

(c) prediction for axial compression (<u>MO</u> theory or <u>CFT</u>). The notation is defined in (a).

observed. More specific information regarding the various approaches has been given by Wentworth and Piper^{97,99}.

D. Infrared Spectra of Cobalt(III) Ammine Complexes

Infrared spectra of a large number of Co(III) ammine complexes have been published^{47,102-105} and theoretical calculations have been performed for the Co-NH₃ system^{106,107} and the octahedral $Co(NH_3)_6^{3+}$ system^{108,109}.

The spectra of Co(III) ammine complexes in the region above 650 cm.⁻¹ (NaCl region) are characterized by the vibration of the NH₃ group. The four bands (or sets of bands) that appear in the NaCl region have been assigned on the basis of a vibrational analysis of the Co-NH₃ system^{106,107}. The N-H stretching vibration is observed in the region of 3200 cm.⁻¹. The three other bands at about 1600, 1300, and 800 cm.⁻¹ are assigned as the NH₃ degenerate deformation, NH₃ symmetric deformation and the NH₃ rocking vibrational frequencies, respectively. It has been found that the three NH₃ deformation frequencies are affected by the nature of the anion present¹⁰², and the changes have been ascribed to hydrogen bonding between the ammine hydrogens and the anions.

The spectra of Co(III) ammine complexes in the region below 650 cm.⁻¹ (CsBr region) are characterized by skeletal vibrations. Generally, spectra of Co(III) ammines in the CsBr region show a set of three weak bands between 450 and 550 cm.⁻¹ and a strong, broad band between 300 and 350 cm.⁻¹. In case of the octahedral hexamminecobalt(III) ion, there

are six skeletal vibrations, of which only two are infrared active: the assymmetric Co-N stretching vibration and the N-Co-N angle of deformation vibration, both of which transform as the T_{1u} representation of the point group O_h .

Block¹⁰⁸ assumed that the NH₃ groups are in weak libration about the Co-N axis and calculated the vibrational frequencies for the $Co(NH_3)_6^{3+}$ system. He concluded that the Co-N stretching vibrational frequency should be in the region of 500 cm.⁻¹, but did not calculate the angle deformation vibrational frequency. Shimanouchi and Nakagawa¹⁰⁹ treated only the CoN₆ octahedron and concluded that the stretching vibrational frequency should be at 464 cm.⁻¹ and the angle deformation vibrational frequency at 329 cm.⁻¹. Similar results were obtained for substituted Co(III) ammines.

From the above theoretical treatments^{108,109}, it is possible to tentatively assign the observed bands of Co(III) ammines in the CsBr region. The set of three weak bands between 450 and 550 cm.⁻¹ is due primarily to the Co-N stretching vibration and the strong band between 300 and 350 cm.⁻¹ is due primarily to the angle deformation vibration. Since both vibrational modes transform as T_{1u} , there is considerable mixing, so that neither vibration is pure stretching or angle deformation. The splitting of the stretching vibration into three bands remains unexplained, although Nakamoto¹¹⁰ has attributed the phenomenon to the influence of the octahedral crystal field.

IV. EXPERIMENTAL

Analytical Methods

<u>Cobalt Analysis</u> - Cobalt was determined spectrophotometrically as the blue tetrathiocyanatocobaltate(II) complex in 50% by volume agetone-water solution.

The cobalt(III) ammine complex was decomposed to give cobalt(II) sulfate by treatment of a 10-12 mg. sample with 5-7 drops of concentrated sulfuric acid followed by gently heating the sample to dryness. The cobalt(II) sulfate was dissolved in a few ml. of water by gentle heating and the solution was transferred to a 100 ml. volumetric flask. The cobalt(II) solution was then treated with 5 ml. saturated ammonium thiocyanate solution, and 50 ml. acetone, and then the flask was filled to the mark with water. The absorbance of the solution at 620 mµ was determined with a Beckman DU spectrophotometer.

The molar absorptivity of the tetrathiocyanatocobaltate (II) complex at 620 m μ was determined by use of a cobalt(II) sulfate solution which had been standardized by the method of Laitinen and Burdett¹¹¹. The solution of the thiocyanate complex obeyed Beer's Law at 620 m μ and had a molar absorptivity of 1817 ± 14. The 1 cm. silica cells used in the determination were recalibrated against each other periodically by use of the standard cobalt(II) sulfate solution.

<u>Nitrogen and Hydrogen Analyses</u> - Nitrogen and hydrogen analyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Michigan.

<u>Water Analyses</u> - Water of hydration was determined by drying <u>in vacuo</u> for 6 hours over P_2O_5 .

Preparation of Compounds

Preparation of μ -amido-decamminedicobalt(III) nitrate - The preparation of the μ -amido-decamminedicobalt(III) nitrate generally followed the procedures given by Werner^{2,19}. A less detailed procedure has also been given by Vannerberg²⁰ The series of reactions used in the synthesis are as follows;

$$4Co(H_20)_6^{2+} + 18NH_3 + O_2(g) + 5SO_4^{2-} + 2H^+ \longrightarrow [(NH_3)_4Co(NH_2, SO_4)Co(NH_3)_4]_2(SO_4)_3 + 2H_2O (1) [(NH_3)_4Co(NH_2, SO_4)Co(NH_3)_4]_2(SO_4)_3 + 6NO_3^- \longrightarrow 2[(NH_3)_4Co(NH_2, SO_4)Co(NH_3)_4] (NO_3)_3(I) + 3SO_4^{2-} (2) [(NH_3)_4Co(NH_2, SO_4)Co(NH_3)_4] (NO_3)_3 + 5C1^- + H_2O \longrightarrow [H_2O(NH_3)_4CONH_2CoC1(NH_3)_4]C1_4(II) + SO_4^{2-} + 3NO_3^- (3) [H_2O(NH_3)_4CONH_2CoC1(NH_3)_4]C1_4 + 4NO_3^- \longrightarrow [NO_3(NH_3)_4CONH_2CoC1(NH_3)_4] (NO_3)_3(III) + 4C1^- (4) [NO_3(NH_3)_4CONH_2CoC1(NH_3)_4] (NO_3)_3 + 2NH_3 \longrightarrow [(NH_3)_5CONH_2CO(NH_3)_5] (NO_3)_4C1(IV) (5) [(NH_3)_5CONH_2CO(NH_3)_5] (NO_3)_5(V) + C1^- (6)$$

Because the synthesis is a very difficult process, the complete procedure is given below.

(a) Preparation of μ -amido- μ -sulfato-octamminedicobalt (III) nitrate trihydrate (compound I, reactions

<u>1 and 2</u>) - One hundred grams of $Co(NO_3)_2 \cdot 6H_2O$ was dissolved in 450 ml. water in a 2000 ml. filter flask and 650 ml. concentrated ammonia was added while the flask was swirled. The solution was oxidized by bubbling air through a 10 mm. glass tube very slowly for 8 hours. The oxidation resulted in a dark brown solution which was allowed to stand overnight (about 14 hours) at room temperature. The solution was cooled in an ice bath and acidified by the dropwise addition of a mixture of 300 ml. concentrated sulfuric acid and 400 ml. water over a period of 4 hours (the ice cooling was maintained throughout this period). When the acidification was complete, the solution was cooled at about -10° C. (in a refrigerator freezing compartment) in a stoppered flask for about 5 hours. The cooled solution was filtered through a medium fritted funnel. The solid obtained was washed with two 100 ml. portions of ethanol and 50 ml. of ether and then was air-dried. The yield of the red solid (crude Vortmann's Sulfate) was 54 g.

The crude Vortmann's Sulfate (54 g.) was stirred thoroughly with 75 ml. concentrated nitric acid and allowed to stand for about 30 minutes. Water (110 ml.) was slowly stirred in and the mixture was filtered through a medium fritted funnel. The solid obtained was washed with four 100 ml. portions of water, two 50 ml. portions of ethanol, 50 ml. of ether, and was then air-dried. The red solid was <u>crude</u> μ -amido- μ -sulfato-octamminedicobalt(III) nitrate and the yield was 20 g.

A pure sample of μ -amido- μ -sulfato-octamminedicobalt(III) nitrate trihydrate, $[(NH_3)_4Co(NH_2,SO_4)Co(NH_3)_4](NO_3)_3\cdot 3H_2O$ compound I, was prepared by washing the crude product with large amounts of water (about 1 liter in 10 to 15 portions), though the yield was considerably reduced because of the compound's solubility in water. <u>Anal</u>. Calc'd.: Co, 19.4. Found: Co, 19.3.

The compound may also be recrystallized from dilute nitric acid.

The infrared spectrum of compound I in the region of sulfate absorption $(900-1200 \text{ cm.}^{-1})$ agreed with that given by Nakamoto, <u>et. al.</u>¹¹². The four sulfate bands were found at 998, 1062, 1109, and 1161 cm.⁻¹.

In an attempt to determine the major product of the oxidation, (as well as to identify the major impurity in the above-mentioned compounds) a portion of the filtrate obtained in the separation of the crude Vortmann's Sulfate was treated with excess sulfuric acid and cooled at -10° C. An orange-yellow crystalline solid separated and was filtered, washed with ethanol, and dried. The compound gave a white precipitate with Ba²⁺ and had absorption peaks at 340 and 478 mµ. The absorptions correspond to the hexamminecobalt(III) sulfate, which could then be regarded as the major product of the oxidation as well as the major impurity in the crude μ -amido- μ -sulfato-octamminedicobalt(III) nitrate. It is also probable that the hexammine was the major impurity in the compounds subsequently obtained in the synthesis.

(b) Preparation of <u>u</u>-amido-6-chloro-6'-aquo-2,2',3,3', 4,4',5,5'-octamminedicobalt(III) chloride tetra-

<u>hydrate (compound II, reaction 3)</u> - (This compound and its complex ion will be referred to henceforth as the "chloroaquo chloride" and the "chloroaquo ion", respectively.) The crude $\underline{\mu}$ -amido- $\underline{\mu}$ -sulfato-octamminedicobalt(III) nitrate (20 g.) was treated with 280 ml. concentrated hydrochloric acid in a 500 ml. erlenmeyer flask and allowed to stand at room temperature for about 25 hours. The mixture, which was blue due to some formation of $\operatorname{CoCl}_4^{2-}$ ion, was filtered through a medium fritted funnel. The solid was washed thoroughly with ethanol to remove all traces of Co(II). It was then washed with about 50 ml. ether and air-dried. The yield was 15.6 g. of the crude chloroaquo chloride.

A sample of the compound was purified as follows: 5 g. of the crude product was dissolved in warm $(45-50^{\circ}C.)$ water, and the solution was filtered. The resulting dark solution was then cooled in a 5°C. refrigerator for a few hours and filtered. Dark purple-red crystals of compound II were obtained, yield 2.2 g. <u>Anal</u>. Calc'd. for $[H_2O(NH_3)_4CONH_2CoCl$ $(NH_3)_4]Cl_4\cdot 4H_2O$: Co, 21.9; N, 23.45; H, 6.75; H₂O, 13.40. Found: Co, 22.5, N, 23.73; H, 6.84; H₂O, 13.36.

(c) Preparation of <u>u</u>-amido-6-chloro-6'-nitrato-2,2',

3,3',4,4',5,5'-octamminedicobalt(III) nitrate

(compound III, reaction 4) - (This compound and its complex ion will be referred to henceforth as the "chloronitrato nitrate" and the "chloronitrato ion", respectively.) The crude chloroaquo chloride (compound II, 12.5 g.) was treated with 185 ml. concentrated nitric acid and the mixture was stirred thoroughly and warmed slightly on a steam bath. After the mixture had cooled, it was filtered through a medium fritted funnel. The solid obtained was dried by sucking air through the filter, and was then washed with 50 ml. ethanol and 20 ml. ether (It is particularly important that <u>all</u> the HNO₃ be removed from the solid before adding ethanol, since cobalt(III) ammines apparently catalyze the oxidation of ethanol by HNO3 in the absence of water. If the HNO₃ is not completely removed, a violent reaction ensues. It is also necessary to add about 50 ml. of water to the filtrate in the filter flask to prevent the occurrence of this reaction in the filtrate.) Air-drying gave 11.5 g. of the crude chloronitrato nitrate (compound III). Attempts to purify this compound by recrystallization from water or dilute nitric acid were unsuccessful. When a fresh aqueous solution of the crude product was treated with Ag⁺, a white precipitate was observed <u>only</u> after heating, and thus the presence of coordinated chloride was demonstrated. (d) Preparation of μ -amido-decamminedicobalt(III)

chloride tetranitrate (compound IV, reaction 5). -Two 5 g. portions of the crude chloronitrato nitrate (compound III) were each treated with 750 ml. liquid ammonia in 1 liter Dewar flasks. The flasks were stoppered and the solutions allowed to stand for 2 days (ammonia was added to maintain the volume of the solutions). The stoppers were then removed and the ammonia was allowed to evaporate slowly (about 2 days). The last traces of ammonia were removed by heating the residues with an infrared lamp.

The solid that remained was transferred to a beaker and treated with about 70 ml. water. The mixture was then warmed gently for 5 minutes on a steam bath and filtered, while still warm, through a medium fritted filter. The reddish-pink solid was washed with ethanol and a little ether, and air-dried. Yield, 4.9 g. of crude μ -amido-decamminedicobalt(III) chloride tetranitrate (compound IV).

(e) Preparation of μ -amido-decamminedicobalt(III)

<u>nitrate (compound V, reaction 6)</u> - One and three tenths grams of the μ -amido-decamminedicobalt(III) chloride tetranitrate (compound IV) were dissolved in 200 ml. of water containing 5 ml. of 3N nitric acid by heating on a steam bath. After the hot solution was filtered, it was allowed to cool slowly to room temperature. Deep red crystals of [(NH₃)₅CoNH₂Co(NH₃)₅](NO₃)₅ (compound V) were obtained, yield 0.5 g. Anal. Calc'd.: Co, 19.2. Found: Co, 19.2, 19.0. <u>Preparation of μ -amido-decamminedicobalt(III) chloride di-</u> <u>hydrate</u> - The chloride tetranitrate (compound IV) was converted to the chloride by saturating an aqueous solution with ammonium chloride. The solid filtered from the solution was recrystallized twice from 5% (by volume) hydrochloric acid. The final product consisted of very fine red needles. <u>Anal</u>. Calc'd. for [(NH₃)₅CoNH₂Co(NH₃)₅]Cl₅·2H₂O: Co, 22.8. Found: Co, 22.6, 23.1.

Stability of Solutions of the Bridged Complexes - Aqueous solutions of all the above compounds were found to decompose within 24 hours, depositing a yellow-brown solid. The chloroaquo chloride displayed the lowest stability, generally decomposing within 1 hour or less. It was found, however, that dilute acid solutions of these complexes were stable for at least a month, if not more. It is therefore probable that the decomposition in aqueous solution is due to attack of the amido bridge, since the bridge is undoubtedly protonated in acid solution.

<u>Preparation of Hexamminecobalt(III) chloride</u> - This compound was prepared by Walton's procedure¹¹³. Large orange crystals. <u>Anal</u>. Calc'd. for $Co(NH_3)_6Cl_3$: Co, 22.0. Found: Co, 22.0.

Spectroscopic Measurements

Absorption spectra of solutions in the near infrared, visible, and ultra-violet regions (200-1000 m μ) were determined on a Cary 14 Spectrophotometer with 1 cm. silica cells. Because of the instabilities of the bridged complexes in aqueous solution, all spectra were determined from freshly prepared solutions.

Infrared absorption spectra in the sodium chloride region $(650-5000 \text{ cm.}^{-1})$ were determined in potassium bromide pellets or Nujol mulls on a Unicam SP-200 Infrared Spectrophotometer. Spectra in the cesium bromide region (250- 650 cm.^{-1}) were determined in Nujol mulls on a Perkin-Elmer 301 Spectrophotometer.

A. <u>Molecular Orbital Calculations for the µ</u>-amido-decammine-<u>dicobalt(III) ion</u>.

<u>Structure</u> - A "linear", D_{4h} structure was assumed for the <u>u</u>amido-decamminedicobalt(III) ion (referred to henceforth as the "decammine ion") for the purposes of the <u>MO</u> calculations, shown in Figure 3. The bond lengths were approximated from Vannerberg's structural determination²⁰ (Figure 1) and are shown in Figure 3. The hydrogen atoms were neglected; the ammine groups and the amido group: were treated as nitrogen atoms and a negative nitrogen ion, respectively. As can be seen in Figure 3, there are three types of equivalent nitrogen atoms in the decammine ion: eight equatorial nitrogen atoms (N_e), two axial nitrogen atoms (N_a), and the bridging nitrogen ion (N_b).

The molecular coordinate system is also shown in Figure 3. The z axis was taken as the fourfold axis and the x and y axes were taken to be parallel to the $Co-N_e$ bonds. The origin was placed at the bridging nitrogen.

The linear structure was assumed for the decammine ion primarily to take advantage of the higher symmetry (relative to Vannerberg's bent structure of C_{2v} symmetry) in factoring the secular determinant in the energy calculation (equation (3A-11). In view of the limitations of the Wolfsberg-Helmholz <u>MO</u> method discussed in Section IIIA, the relative ordering of





the one-electron energy levels should not be affected by the assumption of a structure of higher symmetry. The degenerate levels which occur because of the higher symmetry of the linear structure would be split if the symmetry were lowered to C_{2v} , but this splitting is probably negligible in comparison with other energy differences. In addition, the structure of the decammine ion in solution might approximate the assumed linear structure. In order to predict correctly the polarizations of the electronic transitions in crystals containing the decammine ion, however, it would be necessary to use the symmetry group C_{2v} .

<u>Bonding</u> - In the <u>MO</u> calculations for the decammine ion, only $\underline{\sigma}$ - bonding was considered for the Co-N_e and Co-N_a bonds. The equatorial and axial $\underline{\sigma}$ - bonds are shown in Figure 3 along with the numbering system used in the calculation of the orbital transformations. In the case of the bridge system (Co¹-N_b-Co²) both $\underline{\pi}$ - and $\underline{\sigma}$ - bonds were considered. The orientation of the bridge $\underline{\pi}$ - and $\underline{\sigma}$ - bonds are shown in Figure 3 ($\underline{\sigma}_z$, $\underline{\pi}_x$ and $\underline{\pi}_y$).

The equatorial and axial nitrogen $\underline{\sigma}$ -orbitals were assumed to be hybrid orbitals of the form:

 $\phi(2\sigma) = (\sin \theta)\phi(2s) \pm (\cos \theta)\phi(2p \text{ or } 3d) \quad (5A-1)$

The degree of hybridization was estimated after the manner of Ballhausen and Gray⁶⁴, by minimizing the quantity <u>VSIE $(\theta)/S(\theta)$ </u>, where <u>S(θ)</u> is the overlap between the hybrid orbital and the appropriate cobalt orbital. <u>VSIE (θ) </u> is the valence state ionization energy for different amounts of mixing $\underline{\theta}$, calculated from the relationship:

 $H(2\sigma) = (\sin^2 \theta) H(2s) + (\cos^2 \theta) H(2p)$ (5A-2) where $H(2\sigma)$, H(2s), and H(2p) are the coulomb integrals (the negative of the <u>VSIE</u>) for the hybrid orbital, the pure 2s orbital and the pure 2p orbital, respectively. The minimization of <u>VSIE(θ)/S(θ)</u> gave values of $\theta_e = 0.243$ and $\theta_a = 0.314$ radians for the equatorial and axial nitrogen σ -orbitals, respectively. These values correspond to 5.9% and 9.5% 2scharacter for the equatorial and axial hybrid σ -orbitals, respectively.

The <u>o</u>-orbitals on the bridging nitrogen ion $(\underline{\sigma}_z)$ were assumed to be pure 2s and $2p_z$ atomic orbitals. The 2s orbital was not included in the calculations for reasons to be discussed later. The <u>m</u>-orbitals $(\underline{\pi}_x \text{ and } \underline{\pi}_y)$ on N_b were taken as pure $2p_x$ and $2p_y$ atomic orbitals.

The ligand group orbitals (linear combinations of the atomic or hybrid orbitals of the individual ligand atoms) were determined by use of standard group theoretical technigues^{72,74,82}.

The cobalt 3d, 4s, and 4p atomic orbitals were used in the calculation. The $3d_{z^2}$ and 4s atomic orbitals were assumed to mix according to equation (1) with $\theta = \pi/4$ radians (50% 4s, 50% $3d_{z^2}$). The cobalt group orbitals (linear combinations of the atomic orbitals of the two cobalt atoms) were taken as sum and difference combinations of the atomic orbitals on the two cobalt centers. Thus the cobalt group orbitals had forms such as $(3d_{xy}^1 \pm 3d_{xy}^2)$ and $4p_x^1 \pm 4p_x^2)$, where the superscript indicates the cobalt atom to which the atomic orbitals belong. Metal-metal overlap (which would be extremely small for the decammine ion, since the Co-Co distance is 4.4 Å in the linear structure) was neglected in the normalization of the cobalt group orbitals.

The orbital transformation scheme for the decammine ion is shown in Table I.

<u>Radial Functions</u> - The cobalt 3d, 4s, and 4p functions were taken from the data of Richardson, <u>et</u>. <u>al</u>.^{114,115}, by use of the data for a charge of +1 on the cobalt atom (since the cobalt atoms were assumed to have a charge). The radial functions for the nitrogen 2s and 2p orbitals were calculated from the data of Hartree¹¹⁶. The radial functions used in the calculations are summarized in Table II, where the individual terms have the form of a Slater-type orbital (STO):

$$\Phi_{n}(\mu) = N r^{n-1} e^{-\mu r}$$
 (5A-3)

where <u>n</u> is the principle quantum number, $\underline{\mu}$ is the "Slater exponent" and N is the normalization constant, given by

$$N = [(2\mu)^{2n-1}/(2n)!]^{1/2} \qquad (5A-3a)^{1/2}$$

<u>Group Overlap Integrals</u> - Equations relating the group overlap integrals $(\underline{G_{ij}}'s)$ to simple diatomic overlap integrals $(\underline{S_{ij}}'s)$ were determined by the methods that have been outlined in detail by Bedon, <u>et</u>. <u>al</u>.⁷⁰, Ballhausen¹¹⁷ and

| Repre- senta- tion | Cobalt Orbitals | Ligand Orbitals |
|--------------------------|---|---|
| ^a 1g | $\frac{1}{\sqrt{2}}(4p_{z}^{1} - 4p_{z}^{2})$ | $\frac{1}{\sqrt{2}}(\sigma_{9} + \sigma_{10})$ |
| | $\frac{1}{2}[(4s^{1}+3d_{z^{2}}^{1})+(4s^{2}+3d_{z^{2}}^{2})]$ | $\frac{1}{\sqrt{8}}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6 + \sigma_7 + \sigma_8)$ |
| | $\frac{1}{2}[(4s^1-3d^1_{Z^2})+(4s^2-3d^2_{Z^2})]$ | |
| ^b 1g | $\frac{1}{\sqrt{2}}(3d_{x^{2}-y^{2}}^{1}+3d_{x^{2}-y^{2}}^{2})$ | $\frac{1}{\sqrt{8}}(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4 + \sigma_5 - \sigma_6 + \sigma_7 - \sigma_8)$ |
| ^b 2g | $\frac{1}{\sqrt{2}}(3d_{xy}^1 + 3d_{xy}^2)$ | |
| eg | $\frac{1}{\sqrt{2}}(4p_x^1 - 4p_x^2)$ | $\frac{1}{2}(\sigma_1 - \sigma_3 + \sigma_5 - \sigma_7)$ |
| | $\frac{1}{\sqrt{2}}(4p_{y}^{1} - 4p_{x}^{2})$ | $\frac{1}{2}(\sigma_2 - \sigma_4 + \sigma_6 - \sigma_7)$ |
| | $\frac{1}{\sqrt{2}}(3d_{xz}^{1} + 3d_{xz}^{2})$ | |
| | $\frac{1}{\sqrt{2}}(3d_{yz}^{1} + 3d_{yz}^{2})$ | |
| ^a 2u | $\frac{1}{\sqrt{2}}(4p_{z}^{1} + 4p_{z}^{2})$ | σ _z |
| | $\frac{1}{2}[(4s^1+3d^1_{Z^2})-(4s^2+3d^2_{Z^2})]$ | $\frac{1}{\sqrt{2}}(\sigma_9 - \sigma_{10})$ |
| | $\frac{1}{2}[(4s^1-3d^1_{z^2})-(4s^2-3d^2_{z^2})]$ | $\frac{1}{\sqrt{8}}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 - \sigma_5 - \sigma_6 - \sigma_7 - \sigma_8)$ |
| ^b 1u | $\frac{1}{\sqrt{2}}(3d_{xy}^{1} - 3d_{xy}^{2})$ | |
| ^b 2u | $\frac{1}{\sqrt{2}}(3d_{x^{2}-y^{2}}^{1}-3d_{x^{2}-y^{2}}^{2})$ | $\frac{1}{\sqrt{8}}(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4 - \sigma_5 + \sigma_6 - \sigma_7 + \sigma_8)$ |
| e _u | $\frac{1}{\sqrt{2}}(4\mathbf{p}_{\mathbf{X}}^{1}+4\mathbf{p}_{\mathbf{X}}^{2})$ | $\frac{1}{2}(\sigma_1 - \sigma_3 - \sigma_5 + \sigma_7)$ |
| | $\frac{1}{\sqrt{2}}(4\mathbf{p}_{\mathbf{y}}^{1} + 4\mathbf{p}_{\mathbf{y}}^{2})$ | $\frac{1}{2}(\sigma_2 - \sigma_4 - \sigma_6 + \sigma_8)$ |
| | $\frac{1}{\sqrt{2}}(3d_{xz}^{1} - 3d_{xz}^{2})$ | $\pi_{\mathbf{x}}$ |

 π_{y}

 $\frac{1}{\sqrt{2}}(3d_{yz}^{1} - 3d_{yz}^{2})$

Table I. Orbital transformation scheme for the μ -amidodecamminedicobalt(III) ion in D_{4h} symmetry.

Table II. Radial functions for the atomic orbitals used in the <u>MO</u> calculations^a.

 $\frac{\text{Cobalt}}{\text{R}(3d) = 0.568 \phi_3(5.55) + 0.606 \phi_3(2.10)}$ $R(4s) = -0.02078 \phi_1(26.375) + 0.06920 \phi_2(10.175)$ $-0.1697 \phi_3(4.69) + 1.0118 \phi_4(1.45)$ $R(4p) = 0.01091 \phi_2(11.05) - 0.03681 \phi_3(4.385)$ $+ 1.00061 \phi_4(0.83)$ $\frac{\text{Equatorial and axial nitrogen}}{\text{R}(2s) = \phi_2(2.25)}$ $R(2p) = \phi_2(1.77)$ $\frac{\text{Bridging nitrogen}}{\text{R}(2s) = \phi_2(2.16)}$ $R(2p) = \phi_2(1.42)$

 $a_{\phi_n}(\mu) = N r^{n-1} e^{-\mu r}$.

Ballhausen and Gray¹¹⁸. The expressions were derived by substituting the relevant cobalt and ligand group orbitals in the equation:

$$G_{ij} = \int \psi_i \psi_j d\tau \qquad (5A-4)$$

Equation (4) was then expanded. The approximation of zero overlap between orbitals on atoms not directly bonded to each other was used. This principle may be demonstrated for the case of the overlap between the e_g orbitals $\frac{1}{\sqrt{2}}(4p_x^1 - 4p_x^2)$ and $\frac{1}{2}(\sigma_1 - \sigma_3 + \sigma_5 - \sigma_7)$ by the following transformations:

$$G[e_{g}(\sigma)] = \int \frac{1}{\sqrt{2}} (4p_{x}^{1} - 4p_{x}^{2}) \frac{1}{2} (\sigma_{1} - \sigma_{3} + \sigma_{5} - \sigma_{7}) d\tau \qquad (5A-5a)$$

$$= \frac{1}{2\sqrt{2}} \left[\int 4p_{\mathbf{X}}^{1}(\sigma_{1} - \sigma_{3}) d\tau - \int 4p_{\mathbf{X}}^{2}(\sigma_{5} - \sigma_{7}) d\tau \right] \qquad (5A-5b)$$

$$= \frac{1}{\sqrt{2}} \int 4p\sigma(\sigma_1 - \sigma_3) d\tau \qquad (5A-5c)$$

$$= \frac{2}{\sqrt{2}} \int (4p\sigma) (2\sigma) d\tau \qquad (5A-5d)$$

$$= \sqrt{2}[S(2\sigma, 4p\sigma)] \tag{5A-5e}$$

where 2σ and $4p\sigma$ represent the hybrid ligand atomic orbital and the cobalt 4p orbital, respectively.

The values of the group overlap integrals are given in Table III, in which the <u>MO</u>'s are defined. Interactions not listed in Table III were assumed to have zero overlap (e.g. the overlap of the e_g orbitals $\frac{1}{\sqrt{2}}(3d_{xz}^1 + 3d_{yz}^2)$ and $\frac{1}{2}(\sigma_1 - \sigma_3 + \sigma_5 - \sigma_7)$ was assumed to be zero). The relationships between the <u>Gij</u>'s and <u>Sij</u>'s are listed in Table IV.

| Table III. | Group overlap in dicobalt(III) io | tegrals for the μ -amido-decammine- n. | |
|--|--|--|-----------------|
| Molecular Orbital | Cobalt Orbita | l Ligand Orbital | G _{ij} |
| Σ [a _{1g} (σ ₁)] | $\frac{1}{\sqrt{2}}(4p_{z}^{1} - 4p_{z}^{2})$ | $\frac{1}{\sqrt{2}}(\sigma_{9}+\sigma_{10})$ | 0.090 |
| $\Phi^{[a_{1g}(\sigma_2)]}$ | $\frac{1}{2}$ [(4s ¹ +3d ¹ ₂)+(4s ²) | $+3d_{z^2}^2)]\frac{1}{\sqrt{2}}(\sigma_9+\sigma_{10})$ | 0.177 |
| $\overline{\Phi}[a_{1g}(\sigma_3)]$ | $\frac{1}{2}[(4s^1-3d_{z^2}^1)+(4s^2$ | $-3d_{22}^{2})]\frac{1}{\sqrt{8}}(\sigma_{1}+\sigma_{2}+\sigma_{3}+\sigma_{4}+\sigma_{5}+\sigma_{6}+\sigma_{7}+\sigma_{8})$ | 0.354 |
| ⊈[b _{1g} (σ)] | $\frac{1}{\sqrt{2}}(3d_{x^{2}-y^{2}}^{1}+3d_{x^{2}-y}^{2}$ | $_{2}) \qquad \frac{1}{\sqrt{8}}(\sigma_{1}-\sigma_{2}+\sigma_{3}+\sigma_{4}+\sigma_{5}-\sigma_{6}+\sigma_{7}-\sigma_{8})$ | 0.220 |
| $\mathbb{P}[\mathbf{b}_{2g}(\pi)]$ | $rac{1}{\sqrt{2}}(\operatorname{3d}^1_{xy}+\operatorname{3d}^2_{xy})$ | | • • |
| $\overline{\Phi}_{I}[e_{q}(\sigma)]$ | $\frac{1}{\sqrt{2}}(4p_x^1 - 4p_x^2)$ | $\frac{1}{2}(\sigma_1 - \sigma_3 + \sigma_5 - \sigma_7)$ | 0.127 |
| $\Phi_{II}[e_g(\sigma)]$ | $\frac{1}{\sqrt{2}}(4p_{y}^{1} - 4p_{y}^{2})$ | $\frac{1}{2}(\sigma_2 - \sigma_4 + \sigma_6 - \sigma_8)$ | 0.127 |
| $\Xi_{I}[e_{g}(\pi)]$ | $\frac{1}{\sqrt{2}}(3d^1_{xz}+3d^2_{xz})$ | | •• |
| $\Phi_{\text{II}}[e_{g}(\pi)]$ | $rac{1}{\sqrt{2}}(\operatorname{3d}_{yz}^1+\operatorname{3d}_{yz}^2)$ | • • • • • | •• |
| $\overline{\Phi}[a_{2u}(\sigma_1)]$ | $\frac{1}{\sqrt{2}}(4p_{z}^{1}+4p_{z}^{2})$ | σ _z | 0.034 |
| $\Phi[a_{2u}(\sigma_2)]$ | $\frac{1}{\sqrt{2}}(4p_{z}^{1} + 4p_{z}^{2})$ | $\frac{1}{\sqrt{2}}(\sigma_9 - \sigma_{10})$ | 0.090 |
| $\overline{\Phi}[a_{2u}(\sigma_3)]$ | $\frac{1}{2}$ [(4s ¹ +3d ¹ ₂)-(4s ² | $+3d_{z^{2}}^{2})]$ σ_{z} | 0.3 55 |
| $\overline{\Phi}[a_{2u}(\sigma_4)]$ | $\frac{1}{2}$ [(4s ¹ +3d ¹ ₂)-(4s ² | $+3d_{z^2}^2)] = \frac{1}{\sqrt{2}}(\sigma_9 - \sigma_{10})$ | 0.177 |
| ∑[a _{2u} (σ ₅)] | $\frac{1}{2}[(4s^{1}-3d^{1}_{z^{2}})-(4s^{2}$ | $-3d_{2^{2}}^{2})]\frac{1}{\sqrt{8}}(\sigma_{1}+\sigma_{2}+\sigma_{3}+\sigma_{4}-\sigma_{5}-\sigma_{6}-\sigma_{7}-\sigma_{8})$ | 0.354 |
| Φ[b _{1u} (π)] | $\frac{1}{\sqrt{2}}(3d_{xy}^1 - 3d_{xy}^2)$ | • • • • • | c • |
| Φ[b _{2u} (σ)] | $\frac{1}{\sqrt{2}}(3d_{x^2-y^2}^1-3d_{x^2-y^2}^2)$ | $_{2}) \qquad \frac{1}{\sqrt{8}}(\sigma_{1}-\sigma_{2}+\sigma_{3}-\sigma_{4}-\sigma_{5}+\sigma_{6}-\sigma_{7}+\sigma_{8})$ | 0.220 |
| $\tilde{\Phi}_{I}[e_{u}(\sigma)]$ | $\frac{1}{\sqrt{2}}(4p_{x}^{1} + 4p_{x}^{2})$ | $\frac{1}{2}(\sigma_1 - \sigma_3 - \sigma_5 + \sigma_7)$ | 0.127 |
| $\Phi_{II}[e_u(\sigma)]$ | $\frac{1}{\sqrt{2}}(4p_{y}^{1} + 4p_{y}^{2})$ | $\frac{1}{2}(\sigma_2 - \sigma_4 - \sigma_6 + \sigma_8)$ | 0.127 |
| $\Phi_{I}[e_{u}(\pi)]$ | $\frac{1}{\sqrt{2}}(3d_{xz}^1 - 3d_{xz}^2)$ | $\pi_{\mathbf{x}}$ | 0.086 |
| $\Phi_{\text{II}}[e_u(\pi)]$ | $\frac{1}{\sqrt{2}}(3d_{yz}^1 - 3d_{yz}^2)$ | $\pi_{\mathbf{Y}}$ | 0.086 |
| | | | |

Table IV. The group overlap integrals $(\underline{G}_{\underline{i}\underline{j}} 's)$ for the $\underline{\mu}$ amido-decamminedicobalt(III) ion in terms of atomic overlap. integrals. $(\underline{S}_{\underline{i}\underline{j}} 's)^{a,b}$.

$$G[a_{1g}(\sigma_{1})] = G[a_{2u}(\sigma_{2})] = S(2\sigma, 4p\sigma)$$

$$G[a_{1g}(\sigma_{2})] = G[a_{2u}(\sigma_{4})] = (\sqrt{2}/2)[S(2\sigma, 4s) + S(2\sigma, 3d\sigma)]$$

$$G[a_{1g}(\sigma_{3})] = G[a_{2u}(\sigma_{5})] = (\sqrt{2}/2)[2S(2\sigma, 4s) + S(2\sigma, 3d\sigma)]$$

$$G[a_{2u}(\sigma_{1})] = \sqrt{2}S(2p\sigma, 4p\sigma)$$

$$G[a_{2u}(\sigma_{3})] = S(2p\sigma, 4s) + S(2p\sigma, 3d\sigma)$$

$$G[b_{1g}(\sigma)] = G[b_{2u}(\sigma)] = \sqrt{3}S(2\sigma, 3d\sigma)$$

$$G[e_{g}(\sigma)] = G[e_{u}(\sigma)] = \sqrt{2}S(2p\pi, 3d\pi)$$

^aThe molecular orbitals referred to in the G 's are defined in Table II.

^bThe atomic overlap of orbitals \underline{i} and \underline{j} is written as $\underline{S}_{\underline{ij}} = \underline{S}(\underline{i},\underline{j})$; orbtial \underline{i} refers to ligand atomic orbitals and \underline{j} refers to cobalt atomic orbitals.

Evaluation of the Atomic Overlap Integrals $(S_{ij}'s)$ - The atomic overlap integrals needed for determination of the $G_{ij}'s$ were evaluated by use of tables giving overlap integral values (henceforth, overlap tables) and master formulae given in the literature^{76,119,120}. The relevant radial functions from Table II were substituted in the expression:

$$\mathbf{S}_{ij} = \int \phi_i \phi_j \, d\tau \qquad (5\mathbf{A}-\mathbf{6})$$

and the equation expanded. Each term was then evaluated by use of the overlap tables or master formulae. The overlap tables are given as functions of the two parameters \underline{p} and \underline{t} :

$$p = \left(\frac{\mu_{i} + \mu_{j}}{2}\right) \cdot \frac{R}{a_{0}}$$

$$t = \frac{\mu_{i} - \mu_{j}}{\mu_{i} + \mu_{j}}$$
(5A-7)

where $\underline{\mu_i}$ and $\underline{\mu_j}$ are the <u>STO</u> exponents of orbitals \underline{i} and \underline{j} $(\underline{\mu_i} > \underline{\mu_j})$, \underline{R} is the bond length in $\overset{0}{A}$, and $\underline{a_0}$ is the Bohr radius (0.529 $\overset{0}{A}$). The overlap tables and master formulae given by Jaffe and Doak¹²⁰ for 5s and 5p orbitals were used in the calculation of 4s and 4p overlap integrals, since their tables and formulae were calculated with the assumption of an <u>effective principle quantum number</u>, \underline{n}^* , of 4. The use of an effective quantum number was unnecessary for the 4s and 4p orbitals, because the radial functions were calculated independently^{114,115}. A detailed outline of the calculation of a typical overlap integral has been given by Bedon, <u>et</u>. <u>al</u>.⁷⁰. The values obtained for the S_{ij} 's are listed in Table V.

| Overlap Integral ^a | Type ^b | Value | |
|---|-------------------|-------|--|
| S(20,4s) | e | 0.187 | |
| S(2 σ, 4 pσ) | е | 0.090 | |
| S(20,3d0) | е | 0.127 | |
| S(2σ,4s) | a | 0.071 | |
| S(2 σ, 4 pσ) | a | 0.043 | |
| S(2 σ, 3 dσ) | a | 0.179 | |
| S(2po,4po) | b | 0.034 | |
| S(2po,4s) | b | 0.251 | |
| S(2p σ, 3 dσ) | b | 0.104 | |
| $\mathtt{S}(\mathtt{2}\mathtt{p}\pi,\mathtt{3}\mathtt{d}\pi)$ | b | 0.061 | |
| | | | |

Table V. Atomic overlap integrals (S_ij).

^aThe $\underline{S}_{\underline{ij}}$'s are written as $\underline{S(\underline{i,j})}$ where \underline{i} is the ligand atomic orbital and \underline{j} is the cobalt atomic orbital.

^b<u>e</u> - equatorial, with R = 2.05 Å; 2σ has 5.9% 2s character. <u>a</u> - axial, with R = 1.70 Å; 2σ has 9.5% 2s character.

<u>b</u> - bridging, with R = 2.20 Å; 2σ is a pure 2p orbital.

<u>Valence State Ionization Energies (VSIE)</u> - The <u>VSIE</u> for the cobalt 3d,4s, and 4p orbitals were estimated by means of the procedure outlined by Ballhausen and $\operatorname{Gray}^{121}$. The data for the cobalt <u>VSIE</u> given by Ballhausen and $\operatorname{Gray}^{121}$ were used to determine the values of <u>A</u>, <u>B</u>, and <u>C</u> in the equation:

$$VSIE = Aq^2 + Bq + C \qquad (5A-8)$$

(where <u>q</u> is the charge on the cobalt atom) for different starting configurations. The values of <u>A</u>, <u>B</u>, and <u>C</u> are listed in Table VI for the different starting configurations. The values of the coulomb integrals <u>H(3d)</u>, <u>H(4s)</u>, and <u>H(4p)</u> were then calculated for an assumed configuration $3d^{(9-s-p-q)}$ $4s^{s} 4p^{p}$ with the charge <u>q</u> = $9-\underline{d}-\underline{s}-\underline{p}$ from the relationships¹²¹: - H(3d) = 3d VSIE = $(1-s-p)(3d VSIE:3d^{9}) + s(3d VSIE: 3d^{8} 4s)$ + $p(3d VSIE: 3d^{8} 4p)$ (5A-9a)

-
$$H(4s) = 4s VSIE = (2-s-p)(4s VSIE: 3d^8 4s)$$
 (5A-9b)
+ $(s-1)(4s VSIE: 3d^7 4s^2) + p(4s VSIE: 3d^7 4s 4p)$
- $H(4p) = 4p VSIE = (2-s-p)(4p VSIE: 3d^8 4p)$ (5A-9c)
+ $(p-1)(p VSIE: 3d^7 4p^2) + s(4p VSIE: 3d^7 4s 4p)$

where the <u>VSIE</u> on the right side of the equations are calculated from the data in Table VI. Equations (9a)-(9c) represent an averaging over the different configurations; the sum of coefficients on the right side of each equation is unity.

Ligand <u>VSIE</u> were calculated from the data given by Ballhausen and Gray¹²¹ for neutral N atoms. The coulomb integrals of the equatorial and axial nitrogen $\underline{\sigma}$ -orbitals were calculated from equation (2).

| VSIE | Starting Configuration | А | В | С |
|------------|---------------------------------|-------|--------|-------|
| 3d | 3d ⁹ | 13.05 | 91.15 | 44.80 |
| 3 d | 3d ⁸ 4s | 13.85 | 106.25 | 75.60 |
| 3 d | 3d ⁸ 4p | 13.85 | 105.55 | 88.40 |
| | | | | |
| 4 s | 3d ⁸ 4s | 7.25 | 66.65 | 59.10 |
| 4s | 3d ⁷ 4s ² | 7.25 | 75.75 | 70.50 |
| 4s | 3d ⁷ 4s4p | 7.25 | 71.35 | 84.00 |
| | | | | |
| 4 p | 3d ⁸ 4p | 7.55 | 51.95 | 30.70 |
| 4 p | 3d74p | 7.55 | 60.65 | 40.70 |
| 4 p | 3d ⁷ 4s4p | 7.55 | 60.65 | 40.80 |
| | | | | |

Table VI. VSIE functions for cobalt^a.

^a<u>VSIE(q)</u> = Aq^2 + Bq + C; values of <u>A</u>, <u>B</u> and <u>C</u> are in units of 1000 cm.⁻¹.

.

The <u>VSIE</u> data of Ballhausen and Gray¹²¹ were calculated from Moore's atomic spectral data⁷⁹. The method of calculation has been outlined in detail by Bedon, <u>et. al</u>.⁷⁰.

<u>Energy Calculations</u> - The one electron energy levels of the <u>MO's were calculated</u> by the solution of the secular determinant:

$$|H_{ij} - EG_{ij}| = 0$$
 (5A-10)

Because the symmetry properties of the molecule were used in the construction of the group orbitals, the secular determinant was factored into a series of low-ordered determinants: 2×2 in the case of the $a_{1g}(\sigma_3)$, $b_{1g}(\sigma)$, $e_g(\sigma)$, $a_{2u}(\sigma_1)$, $b_{2u}(\sigma)$, $e_u(\sigma)$, and $e_u(\pi)$ orbitals; 3×3 for the $a_{1g}(\sigma_1)$ and $a_{1g}(\sigma_2)$ orbitals; and 4×4 for the remaining $a_{2u}(\sigma)$ orbitals.

The 2s orbital on the bridging nitrogen (which transforms as the a_{1g} representation) was not considered in the final energy calculation. In general, the amount of mixing of atomic orbitals in an <u>MO</u> is roughly proportional to the overlap and inversely proportional to the coulomb energy difference $(H_{\underline{1}\underline{1}} - H_{\underline{1}\underline{1}})^{66}$. The overlaps of the 2s orbital on $\underline{N}_{\underline{b}}$ with the cobalt a_{1g} orbitals $\frac{1}{\sqrt{2}}(4p_{\underline{z}}^{1} - 4p_{\underline{z}}^{2})$ and $\frac{1}{2}[(4s^{1} + 3d_{\underline{z}2}^{1}) + (4s^{2} + 3d_{\underline{z}2}^{2})]$ were found to be small (0.016 and 0.032, respectively), and the coulomb energy differences between the 2s orbital and the cobalt orbitals are very large (over 110,000 cm.⁻¹). Preliminary calculations including the 2s orbital verified the conclusion that the 2s orbital does not significantly enter into the bonding in the decammine ion; therefore, the 2s orbital was not considered in the final energy calculation.

The values of the cobalt orbital coulomb integrals for the final calculation were calculated assuming a charge, <u>q</u>, of +0.25 and a configuration of $3d^{8 \cdot 25} 4s^{0 \cdot 15} 4p^{0 \cdot 35}$. Ballhausen has shown¹²² that Yamatera's <u>MO</u> treatment of the hexamminecobalt(III) ion⁹⁸ results in a net charge of +0.30 on the cobalt atom. It was therefore decided that a <u>q</u> value not much different from 0.30 should be used. In addition, the criterion given by Gray and Ballhausen⁶⁶ i.e. that the order of the coulomb energy should be $\sigma(\text{ligand}) < \text{nd}(\text{metal})$ < (n+1)s (metal) < (n+1)p(metal) was taken into consideration. Calculations of the coulomb energies for different values of <u>q</u> indicated that the values based on <u>q</u> = +0.25 were the most reasonable. The coulomb energies are listed in Table VII. The coulomb energy of the cobalt $4s3d_{z^2}$ hybrid was calculated from equation (2).

The nitrogen coulomb energies were taken as the negative of the <u>VSIE</u> of the neutral atom, as discussed above. The values are also listed in Table VII.

The resonance integrals, H_{ij}, were estimated from Ballhausen and Gray's geometric mean equation⁶⁴:

$$H_{ij} = F G_{ij} \sqrt{H_{ii} H_{jj}}$$
 (5A-11)

with a value of -2.0 for <u>F</u> in accordance with Ballhausen and Gray⁶⁴ and other authors^{69,70,71,84}. Cotton and Haas⁸⁰ have

Table VII. Coulomb energies used in the MO calculations^a.

<u>Cobalt orbitals^b.-</u> H(3d) = -90.16 $H(4s3d_{2^2}) = -81.94$ H(4s) = -73.71H(4p) = -38.09

Nitrogen orbitals.-

H(2s) = -206.36 H(2p) = -106.36 $H(2\sigma) = -112.26$ (equatorial) $H(2\sigma) = -115.86$ (axial)

^aEnergies in units of 10³ cm.⁻¹.

^bCalculated from equations (5A-9a)-(5A-9c) assuming a charge, <u>q</u>, of +0.25 and a cobalt configuration of $3d^{8} \cdot 2^{5}4s^{0} \cdot 1^{5}4p^{0} \cdot 3^{5}$. shown that an <u>F</u> value of -2.0 results in a low value of 10Dq, in the hexamminecobalt(III) ion and recommend an <u>F</u> value of -2.30. However, they found that an <u>F</u> value of -2.00 gave the best agreement in the case of the hexamminecobalt(II) ion. The <u>F</u> value used in the present calculation should not seriously affect the relative ordering of the energy levels. However, because of the <u>F</u> value approximation and other approximations discussed above and in Section IIIA, agreement of calculated and experimental energy differences would be fortuitous.

B. <u>Vibrational Analysis Calculations (Normal Coordinate</u> <u>Analyses)</u>

The normal coordinate analysis calculations were performed on the Control Data 3600 computer installation of the Michigan State University Computer Laboratory. The FORTRAN program used to perform the calculations was obtained from Dr. L. B. Sims, and is derived from a program written by Schachtscheider^{123,124}.

The program requires the following input data:

- a) The atomic positions (spherical polar or Cartesian coordinates).
- b) The internal coordinates (bond stretching, valence angle bending, out-of-plane wagging, torsional, linear valence angle bending, and in-plane wagging).
- c) A potential field of the <u>generalized valence force</u> <u>field</u> type (<u>GVFF</u>), consisting of interaction constants between internal coordinates.

The \underline{G} matrix is calculated from the equation:

$$\underline{G} = \underline{B} \underline{M}^{-1} \underline{B}' \qquad (5B-1)$$

where $\underline{\underline{M}}^{-1}$ is the diagonal matrix of the reciprocal atomic masses, and $\underline{\underline{B}}$ is the transformation from the Cartesian displacement coordinates $\underline{\underline{X}}$ to the internal coordinates $\underline{\underline{R}}$: $\underline{\underline{R}} = \underline{B}\underline{X}$ (5B-2)

The <u>B</u> matrix elements are computed by the Wilson <u>S</u>-vector technique^{87,125}. The displacements of the atoms are described by use of atomic displacement vectors, one for each atom, so that the internal coordinates are given by:

$$R_{k} = \sum_{t=1}^{n} \overline{S}_{kt} \cdot \overline{\rho}_{t} = \sum_{i=1}^{3n} B_{ki} x_{i}$$
(5B-3)

where $\overline{\underline{S}_{kt}}$ is the vector describing the displacement of atom $\underline{\underline{t}}$ and the $\overline{\underline{\rho}_{t}}$ is the unit displacement vector of atom $\underline{\underline{t}}$. The three $\underline{\underline{B}_{ki}}$'s belonging to atom $\underline{\underline{t}}$ are the components of the vector $\overline{\underline{S}_{k+}}$.

Wilson's unit vector $\overrightarrow{e_{jj}}^{125}$ along the bond between atom <u>i</u> and atom <u>j</u> is expressed in terms of the Cartesian coordinates of these atoms:

$$\vec{e}_{ij} = [(x_j - x_i) \ \vec{i} + (y_j - y_i) \ \vec{j} + (z_j - z_i) \ \vec{k}]/r_{ij}$$
(5B-4)

where $\underline{r}_{\underline{i}\underline{j}}$ is the bond length and $\underline{i}^{>}$, $\underline{j}^{>}$ and $\underline{k}^{>}$ are unit vectors in the <u>x</u>, <u>y</u> and <u>z</u> directions. The <u>S</u>-vectors are then computed by use of Wilson's formulae^{87,125}. For bond stretching between atoms <u>i</u> and <u>j</u>, the $\overline{S}_{kt}^{>}$ are:

$$\vec{s}_{ki} = -\vec{e}_{ij}$$
 $\vec{s}_{kj} = \vec{e}_{ij}$
 $(5B-5)$

For the bending of the angle $\frac{\alpha_{ijl}}{\underline{\alpha_{ijl}}}$ the $\overline{\underline{S}}_{\underline{kt}}^{\flat}$ for atoms \underline{i} , \underline{j} , and \underline{l} are:

$$\overline{s}_{ki}^{*} = \frac{\cos \alpha_{ij1} \overline{e}_{ji}^{*} - \overline{e}_{j1}^{*}}{r_{ij} \sin \alpha_{ij1}}$$

$$\overline{s}_{kj}^{*} = \frac{\cos \alpha_{ij1} \overline{e}_{j1}^{*} - \overline{e}_{ji}^{*}}{r_{j1} \sin \alpha_{ij1}}$$

$$\overline{s}_{k1}^{*} = -(\overline{s}_{ki}^{*} + \overline{s}_{kj}^{*})$$
(5B-6)

where $\underline{\alpha_{ijl}} \neq 180^{\circ}$. The three $\underline{B_{ki}}$'s belonging to atom \underline{t} are then taken as the \underline{x} , \underline{y} , and \underline{z} components of the $\underline{\overline{S}_{kt}}$ and the $\underline{\underline{G}}$ matrix is computed from equation (1).

The solution of the secular equation (see Section IIIB):

$$\underline{G} \underline{F} \underline{L} = \underline{L} \underline{\Lambda}$$
 (5B-7)

is obtained by diagonalizing the product $\underline{G} = \underline{F}$ by use of the Jacobi method for symmetric matrices¹²⁶. Although $\underline{G} = \underline{F}$ is not symmetric, the solution may be accomplished by solving two symmetric problems^{123,124,127}.

Consider the solution of

 $\underline{\mathbf{G}} \ \underline{\mathbf{D}} = \underline{\mathbf{D}} \ \underline{\boldsymbol{\Gamma}} \tag{5B-8}$

where $\underline{\underline{D}}$ is the eigenvector matrix and $\underline{\underline{\Gamma}}$ is the diagonal eigenvalue matrix of $\underline{\underline{G}}$. Since $\underline{\underline{G}}$ is real and symmetric, $\underline{\underline{D}}$ is the orthogonal and the roots are real and positive; then:

 $\underline{G} = \underline{D} \underline{\Gamma} \underline{D}' \tag{5B-9}$
Let \underline{W} be a matrix defined as:

$$\underline{W} = \underline{\Gamma}^{1/2} \underline{D}$$
 (5B-10)

Then:

$$\underline{G} = \underline{W} \underline{W}' \qquad (5B-11)$$

If a matrix \underline{H} , defined by:

$$\underline{\mathbf{H}} = \underline{\mathbf{W}}' \underline{\mathbf{F}} \underline{\mathbf{W}} \tag{5B-12}$$

is considered, the secular equation (7) may be written as:

$$\underline{H} \underline{C} = \underline{C} \underline{\Lambda}$$
 (5B-13)

where <u>C</u> is the orthogonal eigenvector matrix of <u>H</u> and <u>A</u> is the diagonal eigenvalue matrix of <u>H</u>. The elements of <u>A</u> are the $\underline{\lambda_i}$, which are related to the vibrational frequencies, $\underline{\nu_i}$ by:

$$v_{i} = (1/2 \pi c) \sqrt{\lambda}_{i}$$
 (5B-14)

The eigenvector matrix \underline{L} in equation (7) is given by 123, 124, 127:

$$\underline{L} = \underline{W} \underline{C}$$
(5B-15)

and its inverse by:

$$\underline{\mathbf{L}}^{-1} = \underline{\mathbf{C}}^{-1} \underline{\mathbf{W}}^{-1} \tag{5B-16}$$

The transformation matrix \underline{T} , which gives the Cartesian displacements of each atom in each normal coordinate $\underline{Q}_{\underline{i}}$, is computed from the equation^{123,128}:

$$\underline{\mathbf{T}} = \underline{\mathbf{M}}^{-1} \underline{\mathbf{B}}' \underline{\mathbf{F}} \underline{\mathbf{L}} \underline{\boldsymbol{\Lambda}}^{-1} \tag{5B-17}$$

where all the matrices have already been defined.

The computer program, as obtained, was suitable for performing vibrational analyses on molecules of up to 12 atoms. In order to perform the calculations on the decammine

ion (13 atoms), the calculations of the \underline{L} and $\underline{\underline{T}}$ matrices were eliminated.

The vibrational analysis of the decammine ion was performed by separating the system into the linear (D_{4h}) skeletal structure and three sub-molecules with the appropriate local symmetry. Thus, normal coordinate analysis calculations were performed for the decammine ion skeletal vibrations (all hydrogen atoms disregarded); the cobalt-ammine $(Co-NH_3)$ vibrations for equatorial and axial positions; the amido-bridge $(Co-NH_2-Co)$ vibrations; and, for consistency, the hexamminecobalt(III) ion skeletal vibrations. In the above systems, the <u>pattern</u> of the observed spectrum was fit with <u>diagonal</u> force constants only (except for the hexamminecobalt(III) ion).

The neglect of hydrogen vibrations in the treatment of the skeletal vibrations of the decammine and hexamminecobalt-(III) ions (and <u>vice versa</u>) is justified by the frequency separation of the vibrations¹²⁹: the vibrations involving the ammine ligands occur at over 800 cm.⁻¹, while the skeletal vibrations occur below 550 cm.⁻¹.

For each system, symmetry coordinates were used in order to take the symmetry properties of the molecules (or submolecules) into account. The use of symmetry coordinates also removed the redundant coordinates present in each system. The matrices in equations (7) through (16) are then replaced by the appropriate "symmetrized" matrices as described in Section IIIB.

<u>The Cobalt-Ammine (Co-NH₃) Systems</u> - The structure used for the cobalt-ammine system is shown in Figure 4. The angles were assumed to be tetrahedral and the bond length <u>R(N-H)</u> was taken as 1.02 Å¹⁰⁸. The cobalt-nitrogen bond length was taken as 2.05 Å for the treatment of the equatorial cobalt-ammine system and 1.70 Å for the axial cobalt-ammine system²⁰. The system (equatorial or axial) contains ten internal coordinates (see Figure 4): 4 bond stretching coordinates (r_1 , r_2 , r_3 , r_4), three H-N-H angle bending coordinates ($\underline{\alpha_{12}}$, $\underline{\alpha_{13}}$, $\underline{\alpha_{23}}$) and three H-N-Co angle bending coordinates ($\underline{\alpha_{14}}$, $\underline{\alpha_{24}}$, $\underline{\alpha_{34}}$). The potential field was of the <u>GVFF</u> type and only diagonal force constants were used:

$$2V = F_{r}(r_{1}^{2}+r_{2}^{2}+r_{3}^{2}) + F_{r}'(r_{4}^{2}) + F_{\alpha}r_{H}^{2}(\alpha_{12}^{2}+\alpha_{13}^{2}+\alpha_{23}^{2}) + F_{\alpha}'r_{H}r_{Co}(\alpha_{14}^{2}+\alpha_{24}^{2}+\alpha_{34}^{2})$$
(5B-18)

where $\underline{F_r}$ and $\underline{F'_r}$ are the stretching force constants for the N-H and N-Co bonds respectively, and $\underline{r_H}$ and $\underline{r_{Co}}$ are the equilibrium N-H and N-Co distances.

The symmetry of the Co-NH₃ system is C_{3v} . The symmetry coordinates are shown in Table VIII and are similar to those given by Nakagawa and Mizushima¹⁰⁶. The <u>U</u> matrix (see Section IIIB) is obtained from the coefficients of the internal coordinates in the expressions for the symmetry coordinates. All the vibrational modes (the <u>S</u>) shown in Table VIII are infrared and Raman active.



Figure 4. Structure and internal coordinates for the normal coordinate analysis of the cobalt-ammine system. R(N-H) = 1.02 Å, R(Co-N) = 2.05 Å (equatorial or axial), all angles tetrahedral (109⁰28'). Only representative angle bending coordinates are shown.



Figure 5. Structure and internal coordinates for the normal coordinate analysis of the amido-bridge system. $R(N-H) = 1.02 \text{ Å}, R(CO-N) = 2.20 \text{ Å}, \alpha(H-N-H) = 100^{\circ},$ $\alpha(CO-N-CO) = 144^{\circ}$. Only representative angle bending coordinates are shown.

| Table | VIII. | Symmetry | COOI | rdinates | for | the | cobalt-ammine |
|-------|-------|----------|------------------|----------|-------------|-----|---------------|
| | | systems | (C _{3v} | symmetry | <u>/</u>). | | |

| Spec- ies | Vibra- tional Mode | Symmetry Coordinate | Description |
|----------------|--------------------------|--|----------------------------|
| ^A 1 | s ₁ | $(1/\sqrt{3})$ (r ₁ +r ₂ +r ₃) | symmetric N-H stretch |
| | s ₂ | r ₄ | symmetric Co-N stretch |
| | ^S 3 | $(1/\sqrt{6}) (\alpha_{12} + \alpha_{13} + \alpha_{23} - \alpha_{14} - \alpha_{24} - \alpha_{34})$ | symmetric deformation |
| E | s _{4a} | $(1/2)(2r_1 - r_2 - r_3)$ | assymmetric N-H stretch |
| | s_{4b} | $(1/\sqrt{2})$ (r ₂ - r ₃) | |
| | S _{5a} | $(1/2) (2\alpha_{12} - \alpha_{13} - \alpha_{23})$ | degenerate deformation |
| | s _{5b} | (1√2) (a ₁₃ -a ₂₃) | |
| | s _{6a} | $(1/2) (2_{\alpha_{14}} - \alpha_{24} - \alpha_{34})$ | |
| | S _{6b} | (1√2) (α ₂₄ -α ₃₄) | rocking |

The Amido-bridge System $(CO-NH_2-CO)$ - The structure used for the amido-bridge system is shown in Figure 5. The Co-N bond length and the Co-N-Co bond angle were taken as 2.20 Å and 144⁰, respectively²⁰; the N-H bond length was taken as 1.02 Å (as above) and the H-N-H bond angle was approximated as 100⁰. The amido-bridge system also has ten internal coordinates (see Figure 5): 4 bond stretching coordinates (r_1 , r_2 , r_A , r_B); one H-N-H angle bending coordinate ($\frac{\alpha}{12}$); one Co-N-Co angle bending coordinate ($\frac{\alpha}{2B}$); and four H-N-Co angle bending coordinates ($\frac{\alpha}{1A}$, $\frac{\alpha}{2A}$, $\frac{\alpha}{1B}$, $\frac{\alpha}{2B}$.

The potential field was of the <u>GVFF</u> type and only diagonal force constants were considered:

$$2V = F_{r} (r_{1}^{2} + r_{2}^{2}) + F_{r}' (r_{A}^{2} + r_{B}^{2}) + F_{\alpha} r_{H}^{2} (\alpha_{12}^{2}) + F_{\alpha}' r_{Co}^{2} (\alpha_{AB}^{2})$$

$$+ F_{\alpha}'' r_{H} r_{Co} (\alpha_{1A}^{+\alpha} + \alpha_{2A}^{+\alpha} + \alpha_{1B}^{+\alpha} + \alpha_{2B})$$
(5B-19)

where $\underline{F_r}$ and $\underline{F'_r}$ are the stretching force constants, $\underline{F_o}$, $\underline{F'_{\alpha}}$ and $\underline{F''_{\alpha}}$ are the bending force constants, and $\underline{r_H}$ and $\underline{r_Co}$ are the equilibrium N-H and N-Co distances.

The symmetry of the bridge system is C_{2v} and the symmetry coordinates are shown in Table IX (similar coordinates have been given by Nakagawa and Mizushima¹⁰⁶).

All the vibrational modes are Raman active, but only the A_1 , B_1 , and B_2 modes are infrared active.

The Hexamminecobalt(III) Ion - The normal coordinate analysis calculations for the hexamminecobalt(III) ion were done with

| Spec- ies | Vibra- tional Mode | Symmetry Coordinate | Description |
|----------------|--------------------------|---|-----------------------------|
| ^A 1 | s ₁ | $(1/\sqrt{2}) (r_1 + r_2)$ | symmetric N-H stretch |
| | s ₂ | $(1/\sqrt{2})(r_{A} + r_{B})$ | symmetric Co-N stretch |
| | s ₃ | $(1/\sqrt{20}) (4\alpha_{12} - \alpha_{1A} - \alpha_{2A} - \alpha_{1B} - \alpha_{2B})$ | NH_2 bending |
| | s ₄ | ° _{AB} | Co-N-Co bending |
| ^A 2 | s ₅ | $(1/2) (\alpha_{1A}^{-\alpha} - \alpha_{1B}^{-\alpha} - \alpha_{1B}^{+\alpha} - \alpha_{2B}^{-\alpha})$ | NH ₂ twisting |
| ^B 1 | ^S 6 | $(1/\sqrt{2}) (r_{A} - r_{B})$ | assymmetric Co-N stretch |
| | s ₇ | $(1/2) (\alpha_{1A} + \alpha_{2A} - \alpha_{1B} - \alpha_{2B})$ | NH ₂ wagging |
| ^B 2 | ^s 8 | $(1\sqrt{2})(r_1 - r_2)$ | assymmetric N-H stretch |
| | s ₉ | $(1/2) (\alpha_{1A}^{-\alpha} \alpha_{2A}^{+\alpha} \alpha_{1B}^{-\alpha} \alpha_{2B}^{-\alpha})$ | NH ₂ rocking |

Table IX. Symmetry coordinates for the amido-bridge system (C $_{\rm 2v}$ symmetry).

the internal coordinates and symmetry coordinates given by Shimanouchi and Nakagawa¹⁰⁹. A Co-N bond length of 2.05 Å was assumed¹⁰⁸. The potential field was of the <u>GVFF</u> type; in addition to the diagonal force constants, the of**f**-diagonal interactions between Co-N bond stretching coordinates were used in the calculations:

$$2v = F_{r} \sum_{i=1}^{6} r_{i}^{2} + F_{rr'} \sum_{i>j=1}^{6} r_{i} r_{j} + F_{\alpha} r_{N}^{2} \sum_{i>j=1}^{6} \alpha_{ij}^{2} (5B-20)$$

where $\underline{F_r}$ and $\underline{F_{\alpha}}$ are the diagonal stretching and bending force constants respectively, $\underline{F_{rr'}}$ is the off-diagonal stretching interaction constant, and $\underline{r_N}$ is equilibrium Co-N distance.

The hexamminecobalt(III) ion calculations were used as a check on the force constants used for the decammine ion.

The vibrations of the octahedral hexamminecobalt(III) ion transform in O_h as:

$$\Gamma_{v} = A_{1g} + E_{g} + 2T_{1u} + T_{2g} + T_{2u}$$
(5B-21)

The A_{1g} , E_{g} , and T_{2g} vibrations are Raman-active and the T_{2u} vibration is inactive; only the two T_{1u} vibrations (an as-symmetric bond stretching and an angle deformation symmetry coordinate¹⁰⁹) are active in the infrared.

<u>The μ -amido-decamminedicobalt(III) Ion</u> - The linear (D_{4h}) structure used for the decammine ion in the <u>MO</u> calculations was also used in the normal coordinate analysis calculations. The bond lengths were approximated from Vannerberg's data²⁰: $\frac{R(CO-N_e)}{R} = 2.05 \text{ Å; } \frac{R(CO-N_a)}{R} = 1.70 \text{ Å; } \frac{R(CO-N_b)}{R} = 2.20 \text{ Å.}$ Thirty-six internal coordinates were used in the calculationstwelve bond stretching coordinates and 24 angle bending coordinates. The bond stretching coordinates were of three types: equatorial, axial, and bridging Co-N bonds. The angle bending coordinates were also of three types: N_e -Co- N_e , N_e -Co- N_a , and N_e -Co- N_b bond angles. The structure, bond stretching coordinates, and representative angle bending coordinates are shown in Figure 6.

The potential field was of the <u>GVFF</u> type, and only diagonal force constants were used:

$$2V = F_{r}^{e} (r_{1}^{2} + r_{2}^{2} + r_{3}^{2} + r_{4}^{2} + r_{5}^{2} + r_{6}^{2} + r_{7}^{2} + r_{8}^{2}) + F_{r}^{a} (r_{9}^{2} + r_{10}^{2}) + F_{r}^{b} (r_{11}^{2} + r_{12}^{2}) + F_{\alpha}^{e} r_{e}^{2} (\alpha_{12}^{2} + \alpha_{23}^{2} + \alpha_{34}^{2} + \alpha_{14}^{2} + \alpha_{56}^{2} + \alpha_{67}^{2} + \alpha_{78}^{2} + \alpha_{58}^{2}) + F_{\alpha}^{a} r_{e} r_{a} (\alpha_{19}^{2} + \alpha_{29}^{2} + \alpha_{39}^{2} + \alpha_{49}^{2} + \alpha_{5}^{2}, 10^{+\alpha}_{6}^{2}, 10^{+\alpha}_{7}^{2}, 10^{+\alpha}_{8}^{2}, 10) + F_{\alpha}^{b} r_{e} r_{b} (\alpha_{1,12}^{2} + \alpha_{2,12}^{2} + \alpha_{3,12}^{2} + \alpha_{4,12}^{2} + \alpha_{5,12}^{2} + \alpha_{6,12}^{2} + \alpha_{7,12}^{2} + \alpha_{8,12}^{2}) (5B-22)$$

where $\underline{F_r^e}$, $\underline{F_a^e}$, and $\underline{F_r^b}$ are the stretching force constants; $\underline{F_{\alpha}^e}$, $\underline{F_{\alpha}^a}$, and $\underline{F_{\alpha}^b}$ are the bending force constants; $\underline{r_e}$, $\underline{r_a}$, and $\underline{r_b}$ are the equilibrium Co-N_e, Co-N_a and Co-N_b distances, respectively.

Three internal coordinates were not included in the calculations: the two linear bending coordinates connected with the $Co-N_b$ -Co bridge and the torsional coordinate between the two connected $Co-N_5$ groups.

The symmetry coordinates for the decammine ion (in D_{4h}) are shown in Table X. The vibrational modes are listed in



| Spec- ies | Vibra- tional Mode | Symmetry Coordinate |
|-----------------|--------------------------|--|
| A2u | ^S 1 | $\frac{1}{\sqrt{8}}(r_1+r_2+r_3+r_4-r_5-r_6-r_7-r_8})$ |
| | s ₂ | $\frac{1}{\sqrt{2}}(r_9 - r_{10})$ |
| | s ₃ | $\frac{1}{\sqrt{2}}(r_{11} - r_{12})$ |
| | s ₄ | $\frac{1}{4}(a_{19}+a_{29}+a_{39}+a_{49}-a_{1},12-a_{1},12-a_{2},12-a_{4},12$ |
| | | $-\alpha_5, 10^{-\alpha_6}, 10^{-\alpha_7}, 10^{-\alpha_8}, 10^{+\alpha_5}, 12^{+\alpha_6}, 12^{+\alpha_7}, 12^{+\alpha_8}, 12)$ |
| Eu | S _{5a} | $\frac{1}{2}(r_1-r_3-r_5+r_7)$ |
| | s _{5b} | $\frac{1}{2}(r_2-r_4-r_6+r_8)$ |
| | S _{6a} | $\frac{1}{2}(\alpha_{12}-\alpha_{34}-\alpha_{56}+\alpha_{78})$ |
| | s _{6b} | $\frac{1}{2}(a_{23}-a_{14}-a_{67}+a_{58})$ |
| | S _{7a} | $\frac{1}{2}(\alpha_{19}-\alpha_{39}-\alpha_{5},10+\alpha_{7},10)$ |
| | s _{7b} | $\frac{1}{2}(\alpha_{29}-\alpha_{49}-\alpha_{6},10+\alpha_{8},10)$ |
| | s _{8a} | $\frac{1}{2}(\alpha_{1}, 12^{-\alpha_{3}}, 12^{-\alpha_{5}}, 12^{+\alpha_{7}}, 12)$ |
| A _{1g} | s ₉ | $\frac{1}{\sqrt{8}}(r_1+r_2+r_3+r_4+r_5+r_6+r_7+r_8})$ |
| | ^S 10 | $\frac{1}{\sqrt{2}}(r_9 + r_{10})$ |
| | s ₁₁ | $\frac{1}{\sqrt{2}}(r_{11} + r_{12})$ |
| | ^S 12 | $\frac{1}{4}(a_{19}+a_{29}+a_{39}+a_{49}-a_{1},12-a_{2},12-a_{3},12-a_{4},12$ |
| | | +a5,10+a6,10+a7,10+a8,10-a5,12-a6,12-a7,12-a8,12 |

| Table X. | Symmetry coo | ordinates | for the | μ -amido-decamminedi- |
|----------|--------------|----------------------|----------|---------------------------|
| | cobalt(III) | ion (D _{4h} | symmetry | y). |

| Spec- ies | Vibra- tional Mode | Symmetry Coordinate |
|-----------------|--------------------------|--|
| ^B 1g | ^S 13 | $\frac{1}{\sqrt{8}}(r_1 - r_2 + r_3 - r_4 + r_5 - r_6 + r_7 - r_8)$ |
| | ^S 14 | $\frac{1}{4}(a_{19}-a_{29}+a_{39}-a_{49}-a_{1},12+a_{2},12-a_{3},12+a_{4},12 +a_{5},10-a_{6},10+a_{7},10-a_{8},10-a_{5},12+a_{6},12-a_{7},12+a_{8},12$ |
| ^B 2g | ^S 15 | $\frac{1}{\sqrt{8}}(\alpha_{12}-\alpha_{23}+\alpha_{34}-\alpha_{14}+\alpha_{56}-\alpha_{67}+\alpha_{78}-\alpha_{58})$ |
| Eg | S _{16a} | $\frac{1}{2}(r_1-r_3+r_5-r_7)$ |
| | S16b | $\frac{1}{2}(r_2-r_4+r_6-r_8)$ |
| | S _{17a} | $\frac{1}{2}(a_{12}-a_{34}+a_{56}-a_{78})$ |
| | s _{17b} | $\frac{1}{2}(a_{23}-a_{14}+a_{67}-a_{58})$ |
| | ^S 18a | $\frac{1}{2}(a_{19}-a_{39}+a_{5},10-a_{7,10})$ |
| | ^S 18b | $\frac{1}{2}(\alpha_{29}-\alpha_{49}+\alpha_{6,10}-\alpha_{8,10})$ |
| | S _{19a} | $\frac{1}{2}(\alpha_{1,12}-\alpha_{3,12}+\alpha_{5,12}-\alpha_{7,12})$ |
| | ^S 19b | $\frac{1}{2}(\alpha_{2,12}-\alpha_{4,12}+\alpha_{6,12}-\alpha_{8,12})$ |
| ^B 1u | s ₂₀ | $\frac{1}{\sqrt{8}}(\alpha_{12}-\alpha_{23}+\alpha_{34}-\alpha_{14}-\alpha_{56}+\alpha_{67}-\alpha_{78}+\alpha_{58})$ |
| ^B 2u | s ₂₁ | $\frac{1}{\sqrt{8}}(r_1-r_2+r_3-r_4-r_5+r_6-r_7+r_8})$ |
| | ^S 22 | $\frac{1}{4}(a_{19}-a_{29}+a_{39}-a_{49}-a_{1},12+a_{2},12-a_{3},12+a_{4},12$ |
| | | -a5,10+a6,10-a7,10+a8,10+a5,12-a6,12+a7,12-a8,12) |

Table X. (Continued).

.

order of their activity: infrared - A_{2u} and E_{u} ; Raman - A_{1g} , B_{1g} , B_{2g} , and E_{g} ; inactive - B_{1u} and B_{2u} .

.

VI. RESULTS AND DISCUSSION

A. Synthesis

The compound $\underline{\mu}$ -amido-decamminedicobalt(III) nitrate (decammine nitrate) was prepared following Werner's procedures^{2,19}. A problem arose in connection with the reaction of the $\underline{\mu}$ -amido- $\underline{\mu}$ -sulfato-octamminedicobalt(III) nitrate ("sulfato nitrate") with concentrated hydrochloric acid (reaction 3, Section IV). Repeated attempts to remove the sulfate bridge under a variety of conditions (heating, different acids and acidities) failed when the pure sulfato nitrate was used. However, when the <u>crude</u> sulfato nitrate (see Section IV) was used in preparation, the reaction proceeded without complications. The difficulty in reacting the pure sulfato nitrate is apparently due to it being in microcrystalline form, which does not dissolve easily in acid.

The compound $[H_2O(NH_3)_4CoNH_2CoCl(NH_3)_4]Cl_4$ ("chloroaquo chloride") obtained from the crude sulfato nitrate was therefore also used in the crude form. The contaminant is most likely the hexamminecobalt(III) ion (see Section IV). Attempts to purify the chloroaquo chloride generally resulted in precipitation of the contaminant with the product. In some cases (recrystallization from water), the contaminant remained in solution, but a mixture of a purple-red compound (chloroaquo chloride) and a blue-red compound (thought to be

 μ -amido- μ -hydroxo-octamminedicobalt(III) chloride) was obtained. In only one case was the purification successful; the procedure and analytical data are reported in Section IV.

The reaction of the crude chloroaquo chloride with concentrated nitric acid produced the compound $[(NO_3)(NH_3)_4CoNH_2CoCl(NH_3)_4](NO_3)_3$ ("chloronitrato nitrate") in crude form (reaction 4, Section IV). Attempts at purification by various means failed; therefore the crude form was used in the preparation of the decammine nitrate (reactions 5 and 6, Section IV). The successful preparation of the decammine nitrate tends to verify the formulation of the chloronitrato nitrate.

B. Electronic Spectra

The electronic spectral data for the bridged compounds prepared in this investigation are given in Table XI. The perchlorate salt of the μ -amido- μ -sulfato-octamminedicobalt(III, ion was prepared by treatment of the sulfato nitrate with 70% perchloric acid. The spectrum of the chloronitrato nitrate was determined by use of a crude sample, so that the reported molar absorptivities are less than the actual values.

The bands in the spectra of the decammine nitrate and the chloroaquo chloride were analyzed by fitting them to a gaussian error-curve¹³⁰ of the form:

$$\epsilon = \epsilon_{\max} \exp \left[-\left(\frac{v - v_{\max}}{\theta}\right)\right]$$
 (6B-1)

where $\underline{\epsilon}$ and $\underline{\epsilon}_{\max}$ are the molar absorptivities at \underline{v} and \underline{v}_{\max} and θ is given by:

| Compound | Sol- vent | ^v max x10 ⁻³ cm. ⁻¹ | Molar Absorp- tivity |
|---|---|--|----------------------------|
| $[(\mathrm{NH}_3)_5\mathrm{CONH}_2\mathrm{CO}(\mathrm{NH}_3)_5](\mathrm{NO}_3)_5$ | H ₂ O | 19.74 | 412 |
| | | 28.01 | 729 |
| | | 38.90 | 22000 |
| | 0.1N | 19.74 | 409 |
| | HNO ₃ | 27.93 | 673 |
| | | 38.83 | 22000 |
| $[H_2O(NH_3)_4CONH_2CoCl(NH_3)_4]Cl_4$ | 0.1N | 14.20 | 57 |
| | HCI | 20.32 ^a | 169 |
| | | 33.9 | 3340 |
| $[\mathrm{NO}_{3}(\mathrm{NH}_{3})_{4}\mathrm{CONH}_{2}\mathrm{CoCl}(\mathrm{NH}_{3})_{4}](\mathrm{NO}_{3})_{3}^{\mathrm{b}}$ | H ₂ O | 14.39 | (39) |
| | | 20.66° | (152) |
| | | 33.8 | (2580) |
| $[(\mathrm{NH}_3)_4\mathrm{Co}(\mathrm{NH}_2,\mathrm{SO}_4)\mathrm{Co}(\mathrm{NH}_3)_4](\mathrm{ClO}_4)_3^\mathrm{d}$ | H ₂ O | 18.69 | 230 |
| | | 27.25 | 401 |
| | | (36) ^e | (3000) ^e |
| $[Co(NH_3)_6]^{3+f}$ | <u>, , , , , , , , , , , , , , , , , , , </u> | 21.05 | 60 |
| | | 29.50 | 55 |

Table XI. Electronic spectra of some bridged complexes.

^aBroad band, see Figure 8.

^bSpectrum determined using crude compound; reported molar absorptivities are therefore low.

^CSimilar to band in chloroaquo chloride (Figure 8).

^dPrepared by treatment of the nitrate with 70% HClO₄.

eShoulder.

fData from reference 91.

$$\theta = \delta / \ln 2 \qquad (6B-1a)$$

where $\underline{\delta}$ is the half-width of the band. The <u>oscillator strength</u>, <u>f</u>, of each band was obtained from the relation¹³⁰:

$$f = 9.20 \times 10^{-9} \cdot \epsilon_{\max} \delta \qquad (6B-2)$$

In the case of the first band of the decammine nitrate ($v_{max} = 19,740 \text{ cm}^{-1}$) and all the chloroaquo chloride bands, an unsymmetrical gaussian error-curve was assumed in order to fit the band: different half-widths, $\delta(+)$, and $\delta(-)$ for $v > v_{max}$ and $v < v_{max}$, respectively, were used. The oscillator strength was calculated from equation (2) where δ is replaced by $\frac{1}{2}(\delta(+) + \delta(-))$.

The spectrum of the decammine nitrate is shown in Figure 7 (solid line). The dashed curves indicate the curves calculated from equation (1). The parameters used for the Gaussian analysis are shown in Table XII.

In the case of the decammine nitrate, the band in the ultraviolet region ($v_{max} = 38,900 \text{ cm.}^{-1}$) could be resolved into two bands (IIIa and IIIb in Table XII). It is probable that a weaker third band at a lower frequency contributes to the observed band, since the low frequency end of the band could not be fitted exactly with Bands IIIa and IIIb.

The spectrum of the chloroaquo chloride is shown in Figure 8 (solid line) along with the resolved curves (dashed curves). No attempt was made to analyze the band in the ultraviolet ($v_{max} = 33,900 \text{ cm.}^{-1}$) since it is actually a shoulder on a much more intense band. The parameters obtained from the gaussian analyses are shown in Table XIII.





Figure 8. The electronic spectrum of the chloroaquo chloride $([H_2O(NH_3)_4CONH_2CoCl(NH_3)_4]Cl_4)$ in 0.1N HCl. The solid curve is the experimental spectrum; the dashed curves are the resolved bands.

| Band | $v_{\rm max}$ x10 ⁻³ cm ⁻¹ | [€] max | halfwidth (or $\delta(+), \delta(-)$), | f ^a |
|------|---|------------------|--|----------------|
| | | | | |
| I | 19.8 | 420 | 1700,1450 | 0.006 |
| II | 28.0 | 690 | 1900 | 0.012 |
| IIIa | 38.8 | 14000 | 2800 | 0.36 |
| IIIb | 39.3 | 7500 | 1600 | 0.11 |

Table XII. Parameters for the gaussian analysis of the electronic spectrum of $[(NH_3)_5CONH_2Co(NH_3)_5](NO_3)_5$ in water.

^aOscillator strength, from equation (6B-2).

Table XIII. Parameters for the gaussian analysis of the electronic spectrum of $[H_2O(NH_3)_4CoNH_2CoCl(NH_3)_4]Cl_4$ in 0.1N HCl.

| Band | v_{max} x10 ⁻³ cm. ⁻¹ | ^e max | δ(+) cm | δ(-) -1 | f ^a |
|------|--|------------------|------------|------------|----------------------|
| I | 14.2 | 56.9 | 1300 | 1000 | 6×10^{-4} |
| II | 18.5 | 135. | 1450 | 1400 | 1.8×10^{-3} |
| III | 21.0 | 145. | 1350 | 1300 | 1.8×10^{-3} |

^aOscillator strength, from equation (6B-2).

<u>Results</u> - The results of the molecular orbital calculations are shown in Table XIV. The energies were caluclated by solving the secular determinant:

$$|H_{ij} - EG_{ij}| = 0$$
 (6C-1)

The values used for the Coulomb integrals $(\underline{H_{ii}})$ have been given in Table VII, and the group overlap integrals have been given in Table III. The resonance integrals $(\underline{H_{ij}})$ were estimated from the relationship:

$$H_{ij} = -2.0 G_{ij} \sqrt{H_{ii} H_{jj}}$$
 (6C-2)

The coefficients of the <u>MO</u>'s were calculated by substitution of the energy values in the secular equations:

$$\sum_{i=1}^{N} (H_{ij} - EG_{ij}) c_{i} = 0 \quad (j = 1, 2, ..., N) \quad (6C-3)$$

and application of the normalization condition:

$$\Sigma c_i^2 + 2\Sigma c_i c_j G_{ij} = 1$$
 (6C-4)

The population analysis was performed by use of the equation:

POP (ni) =
$$c_{ni}^2 + \sum_{i \neq j} c_{ni} c_{nj} G_{ij}$$
 (6C-5)

(see Section IIIa). The input coulomb energies were calculated for a cobalt atom charge of +0.25 and configuration of $3d^{8} \cdot 25 \ 4s^{0} \cdot 15 \ 4p^{0} \cdot 35$; the population analysis of the results reported in Table XIV give a cobalt atom charge of +1.24 and a configuration of $3d^{6} \cdot 94 \ 4s^{0} \cdot 46 \ 4p^{0} \cdot 36$. The disagreement of input and output values of the charge and

Table XIV. Energy levels and molecular orbital coefficients for the μ -amido-decamminedicobalt(III) ion. Calculated for a charge of +0.25 for the cobalt atoms (see Table VII).

| | -E, | Molec | ular Or | bital (| Coeffic | lents ^a |
|--|--------------------------|-----------------|---------|----------------|----------------|---------------------|
| Orbitals | | ^c 3d | °4p | с _е | c _a | с _р |
| $Ia_{1g}(\sigma), Ia_{2u}(\sigma)$ | 125.1 | 0.421 | • • • | 0.770 | • • • | • • • |
| $IIa_{2u}(\sigma)$ | 123.6 | 0.302 | 0.353 | • • • | 0.748 | 0.297 |
| $Ib_{1q}(\sigma), Ib_{2u}(\sigma)$ | 121.8 | 0.444 | • • • | 0.804 | • • • | • • • |
| $IIa_{1g}(\sigma)$ | 120.3 | 0.101 | 0.346 | ••• | -1.006 | • • • |
| $IIIa_{2u}(\sigma)$ | 115.2 | -0.094 | 0.522 | a e e | 0.664 | -0.492 |
| $Ie_{\sigma}(\sigma), Ie_{u}(\sigma)$ | 112.4 | ••• | 0.031 | 0.996 | • • • | • • • |
| $ie_u(\pi)$ | 109.0 | 0.358 | • • • | ••• | • • • | 0.903 |
| $b_{2q}(\pi), b_{1u}(\pi), e_{q}(\pi)$ | 90.2 | 1.000 | • • • | • • • | • • • | ••• |
| $IIe_{u}(\pi)$ | 86.0 | 0.946 | • • • | ••• | • • • | -0.417 |
| IIIa _{1g} (σ) | 71.4 | 0.964 | 0.089 | ••• | • • • | 0.463 |
| $\text{IIb}_{1q}(\sigma), \text{IIb}_{2u}(\sigma)$ | 70.4 | 0.425 | • • • | 0.635 | • • • | ••• |
| $IVa_{1g}(\sigma), IVa_{2u}(\sigma)$ | 41.9 | 0.859 | • • • | 0.900 | • • • | ••• |
| $Va_{1q}(\sigma)$ | 36.9 ^b | • • • | • • • | ••• | • • • | 0 8 4 |
| $IIe_{q}(\sigma), IIe_{u}(\sigma)$ | 36.2 | • • • | 1.008 | 0.159 | ••• | • • • |
| $va_{2u}(\sigma), VIa_{2u}(\sigma)$ | 33.7 ^b | ••• | • • • | ••• | | 8 9 <i>e</i> |

^a c_{3d} = cobalt 3d orbital coefficient (sd hybrid for a_{1g} and a_{2u} orbitals); c_{4p} = cobalt 4p orbital coefficient; c_e = equatorial σ -orbital coefficient; c_a = axial σ -orbital coefficient; c_b = bridge orbital coefficient (σ_z for a_{2u} (σ) orbitals, π_x and π_y for $e_u(\pi)$ orbitals).

^bCoefficients not calculated.

configuration will be discussed below. The ground state configuration used for the population analysis is derived by assigning the 38 electrons of the system (12 from the 2 cobalt atoms, 6 from the bridging amido group, 20 from the 10 ammine groups) to the lowest lying orbitals:

$$\begin{bmatrix} [Ia_{1g}(\sigma), Ia_{2u}(\sigma)]^{4} [IIa_{2u}(\sigma)]^{2} [Ib_{1g}(\sigma), Ib_{2u}(\sigma)]^{4} [IIa_{1g}(\sigma)]^{2} - \\ [IIIa_{2u}(\sigma)]^{2} [e_{g}(\sigma), Ie_{u}(\sigma)]^{8} [Ie_{u}(\pi)]^{4} [b_{2g}(\pi), b_{1u}(\pi), e_{g}(\pi)]^{8} - \\ [IIe_{u}(\pi)]^{4}] \equiv [CORE]^{26} [b_{2g}(\pi), b_{1u}(\pi), e_{g}(\pi)]^{8} [IIe_{u}(\pi)]^{4} = ({}^{1}A_{1g}) \\ (6C-6) \end{bmatrix}$$

The molecular orbital energy level diagram that is proposed on the basis of the results given in Table XIV is shown in Figure 9. The proposed ordering in Figure 9 differs from the ordering obtained from the calculations only in the relative positions of the $[IIb_{1g}(\sigma), IIb_{2u}(\sigma)]$ and $IIIa_{1g}(\sigma)$ levels; the reasons will be discussed below.

Bonding - The bonding orbitals are of some interest. The equatorial ammine groups (designated $\underline{N_e}$) are bonded to the cobalt atoms through the $Ia_{1g}(\sigma)$, $Ia_{2u}(\sigma)$, $Ib_{1g}(\sigma)$, $Ib_{2u}(\sigma)$, $Ie_g(\sigma)$, and $Ie_u(\sigma)$ orbitals; these orbitals are similar in form to those obtained for $\underline{\sigma}$ -bonding in octahedral compounds¹³¹, and require no further comment. The axial ammine groups (designated $\underline{N_a}$) are $\underline{\sigma}$ -bonded to the cobalt atoms through a combination of the cobalt $4s3d_z^2$ hybrids and $4p_z$ orbitals in the $IIa_{1g}(\sigma)$ orbital. The $\underline{N_a}$ are also involved in the $IIa_{2u}(\sigma)$ and $IIIa_{2u}(\sigma)$ orbitals, which also involve the cobalt-nitrogen-cobalt bridge $\underline{\sigma}$ -bonds. The $IIa_{2u}(\sigma)$ has roughly cylindrical shape which encompasses the N_a -Co- N_b -Co- N_a (N_b is the amido group) axis; from the relative magnitudes of the

| | $Va_{2u}(\sigma), VIa_{2u}(\sigma)$ | | |
|----------------------------|---|---|---------|
| | $va_{1g}(\sigma), IIe_{g}(\sigma), IIe_{u}(\sigma)$ | | |
| | $IVa_{1g}(\sigma), IVa_{2u}(\sigma)$ | | |
| 4p | | | |
| | IIIa _{1g} (σ) | | |
| | $\mathtt{IIb}_{1q}(\sigma),\mathtt{IIb}_{2u}(\sigma)$ | | |
| <u>4s</u> | | | |
| <u>4s3d</u> z ² | | | |
| | $IIe_u(\pi)$ | | ↑ |
| 3 d | $b_{2g}(\pi), e_{g}(\pi), b_{1u}(\pi)$ | | |
| | $le_u(\pi)$ | $\frac{2p(\sigma_z,\pi_x,\pi_y)}{2p(\sigma_z,\pi_x,\pi_y)}$ | E |
| | $Ie_{g}(\sigma), Ie_{u}(\sigma)$ | $2\sigma(equatorial)$ | |
| | IIIa _{2u} (σ) | $2\sigma(axial)$ | |
| | IIa _{1g} (σ) | | |
| | $\mathtt{Ib}_{1g}(\sigma), \mathtt{Ib}_{2u}(\sigma)$ | | |
| | ΙΙa_{2u}(σ) | | |
| | $Ia_{1g}(\sigma), Ia_{2u}(\sigma)$ | | |
| Co orbitals | molecular orbitals | ligand orbitals | |

Figure 9. Proposed molecular orbital energy level diagram for the μ -amido-decamminedicobalt(III) ion (not to scale).

coefficients (Table XIV) it can be estimated that the two electrons in this orbital are located principally in the Co-N_a bonds. The IIIa_{2u}(σ) orbital is also of cylindrical shape, but has a somewhat higher electron density in the Co-N_b bonds. It seems, therefore, that the Co-N_a $\underline{\sigma}$ -bonds acquire additional stabilization at the expense of the Co-N_b bonds; this accounts for the closeness of the axial ammine groups (1.70 Å) in comparison with the equatorial ammine groups (2.05 Å). The extra stability of the Co-N_a $\underline{\sigma}$ bonds also accounts for the relatively large Co-N_b distance (2.2 Å); apparently $\underline{\pi}$ -bonding adds very little stability to the bridge.

The $b_{2g}(\pi)$, $b_{1u}(\pi)$, and $e_g(\pi)$ orbitals are non-bonding orbitals with the electron density completely localized in the cobalt 3d orbitals. The $IIe_u(\pi)$ orbital is an antibonding π -orbital with the electrons localized principally in the cobalt $3d_{xz}$, $3d_{yz}$ orbitals.

The relative magnitudes of the coefficients given in Table XIV indicate that in almost all cases the bonds show appreciable covalency. Fenske⁸⁴, however, has stated that "appreciable covalency is an automatic consequence of the assumptions of the <u>MO</u> method. Whether this conforms to physical reality is highly debatable." In the case of the decammine ion, it is indeed probable that the coefficients obtained in the calculation overestimate the covalency and that the bonding is principally ionic. Consideration of the relative magnitudes of the coefficients in the IIa_{2u}(σ) and IIIa_{2u}(σ) orbitals leads to the conclusion that the bonds involved in bridging (the Co-N_b bonds) are <u>more ionic</u> than the cobalt-ammine (Co-N_a or Co-N_e) bonds. It is probable that the assumption of sp hybridization for the <u>o</u>-bonding orbital of <u>N_b</u> (rather than the pure <u>p</u> orbital used in the calculations) would result in greater covalency in the Co-N_b bond (due to greater overlap); it is questionable, however, whether greater covalency would conform to physical reality. The proposed high ionic character for the Co-N_b bond is consistent with the chemical stability of the Co-NH₂-Co bridge system in spite of the relatively large Co-N_b bond length (2.2 Å).

<u>Ion</u> - The spectrum of the decammine ion is shown in Figure 7 and the numerical data are given in Tables XI and XII. The spectrum consists of two bands of moderate intensity with maxima at 19,740 and 28,010 cm.⁻¹ (Bands I and II, respectively) and an extremely intense charge transfer band (Band III) at 38,900 cm.⁻¹. Bands I and II correspond to the two bands in the spectrum of the mononuclear hexamminecobalt(III) ion (see Table XI) and can be assigned as $d \rightarrow d$ transitions.

The Electronic Spectrum of the μ -amido-decamminedicobalt(III)

The intensities of Bands I and II are significantly greater than the intensities of the corresponding hexamminecobalt(III) band. It is therefore probable that the decammine ion bands are due to <u>symmetry-allowed</u> transitions (the hexamminecobalt (III) bands are symmetry forbidden and acquire intensity from vibronic interactions).

The ground state of the decammine inn has been given in equation (6); the highest occupied orbitals $(b_{2q}(\pi), b_{1u}(\pi),$ $e_{\alpha}(\pi)$ and $e_{u}(\pi)$ are all principally 3d levels and the transitions accounting for Bands I and II should originate from them. Consideration of the symmetry properties of the orbitals listed in Table XIV and the energy differences derived from the data in this table shows that only two transitions of the right order of magnitude in energy are symmetry allowed: $\text{IIe}_{u}(\pi) \rightarrow \text{IIb}_{1g}(\sigma)({}^{1}\text{A}_{1g} \rightarrow {}^{1}\text{E}_{u}^{a}) \text{ and } \text{IIe}_{u}(\pi) \rightarrow$ IIIa_{1q}(σ)(¹A_{1q} \rightarrow ¹E^b_u) (E^a_u and E^b_u are different excited states having E_u symmetry). The relative ordering of the $[IIb_{1q}(\sigma), IIb_{2u}(\sigma)]$ and the $IIIa_{1q}(\sigma)$ orbitals is therefore of great importance for the assignment of the transitions for Bands I and II. The MO calculations reported in Table XIV are of little aid in this respect since the calculated energies of these orbitals are approximately equal; therefore other factors must be considered.

The IIIa_{1g}(σ) orbital is principally composed of the axially symmetric cobalt $4s3d_{z^2}$ hybrids, while the IIb_{1g}(σ) and IIb_{2u}(σ) orbitals are principally composed of the cobalt $3d_{x^2-y^2}$ orbitals. From a qualitative crystal field viewpoint, it would be expected that the closer approach of the axial ammine groups (1.7 Å) would destabilize the axially symmetric $4s3d_{z^2}$ hybrids relative to the $3d_{x^2-y^2}$ orbitals. Thus the ordering of the <u>MO</u>'s would be $a_{1g}(\sigma) > b_{1g}(\sigma)$, $b_{2u}(\sigma)$. Bands I and II of the decammine ion spectrum are then assigned as follows:

Band I:
$$IIe_{u}(\pi) \longrightarrow IIb_{1g}(\sigma) ({}^{1}A_{1g} \longrightarrow {}^{1}E_{u}^{a})$$

Band II: $IIe_{u}(\pi) \longrightarrow IIIa_{1g}(\sigma) ({}^{1}A_{1g} \longrightarrow {}^{1}E_{u}^{b})$ (6C-7)

The ordering arrived at above has been taken into account in the construction of the proposed \underline{MO} energy level diagram (Figure 9).

The ordering of the 3d orbital levels in Figure 9 corresponds to the ordering given in Figure (2c) for the case of axial compression for tetragonal Co(III) complexes. Each cobalt atom in the decammine ion is in a tetragonal environment of C_{4v} symmetry. The proposed ordering of 3d levels indicate that axial compression (by the axial ammine groups) is the principal tetragonal distortion in spite of the elongation exhibited by the $Co-N_h$ bond. Bands I and II may be assigned as the sum of separate transitions on each cobalt atom. Band I would then be assigned as the sum of the two $e \rightarrow b_1 (d_{xz}, d_{yz} \rightarrow d_{x^2-y^2})$ transitions and Band II as the sum of the e \rightarrow a₁ (d_{xz}, d_{yz} \rightarrow d_{z²}). This viewpoint (separate d -> d transitions for each cobalt atom) may be profitably applied to the spectrum of the chloroaquo ion (Figure 9, Table XIII), which will be discussed separately. The notation of the C_{4v} symmetry group will be used henceforth in discussions involving the "separated transitions" viewpoint.

The charge transfer band in the decammine ion spectrum $(38,900 \text{ cm.}^{-1})$ is more easily assigned. Consideration of the orbital symmetries in the <u>MO</u> diagram (Figure 9) and the

e

D

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energy difference derived from Table XIV lead to three allowed charge transfer transitions of the $L \rightarrow M$ (reduction) type. In order of decreasing energy, the transitions are:

$$IIIa_{2u}(\sigma) \longrightarrow IIIa_{1g}(\sigma) ({}^{1}A_{1g} \rightarrow {}^{1}A_{2u})$$
$$Ie_{u}(\sigma) \longrightarrow IIIa_{1g}(\sigma) ({}^{1}A_{1g} \rightarrow {}^{1}E_{u}^{C}) \qquad (6C-8)$$
$$Ie_{u}(\pi) \longrightarrow IIIa_{1g}(\sigma) ({}^{1}A_{1g} \rightarrow {}^{1}E_{u}^{d})$$

The observed charge transfer band can be resolved into two separate bands (Table XII); the disagreement in the observed and calculated line shape on the low frequency side of the band indicates that a third band at lower frequency is at least possible. The three bands would then be assigned to the transitions given in equation (8). It should be noted, however, that the two (or three) observed bands assigned as the charge transfer transfer transitions may not all be due to the decammine ion; since an extremely low concentration (about 3×10^{-5} M) was necessary to observe the spectrum in this region, one of the bands may be due to an hydrolysis or decomposition product of the decammine ion. Thus, while the observed charge transfer band may be assigned as the sum of the transitions given in equation (8), it is not possible to specifically assign each resolved band.

The effect of lowering the symmetry to C_{2v} (Vannerberg's structure²⁰, Figure 1) on the above assignments must be examined. The correlation of the D_{4h} representations with C_{2v} representations are obtained from the tables given by Wilson, Decius and Cross¹³²; the principal axis is taken as the <u>x</u>

axis in Figure 3 (the C'_2 operation in D_{4h}) since this axis would become the major axis of the "bent" structure (Figure 1). One effect of the lower symmetry is the splitting of the $E(D_{4h})$ representations: $e_g(D_{4h}) \rightarrow a_2(C_{2v}) + b_2(C_{2v})$, $e_u(D_{4h}) \rightarrow a_1(C_{2v}) + b_1(C_{2v})$. The other levels of interest (d levels) transform as follows in C_{2v} : $b_{2g}(D_{4h}) \rightarrow b_1(C_{2v})$, $b_{1u}(D_{4h}) \rightarrow a_2(C_{2v})$, $b_{1g}(D_{4h}) \rightarrow a_1(C_{2v})$, $b_{2u}(D_{4h}) \rightarrow b_2(C_{2v})$, $a_{1g}(D_{4h}) \rightarrow a_1(C_{2v})$.

The effect of lowering the symmetry to C_{2v} , then, produces the possibility of more allowed transitions: transitions from the non-bonding orbitals $(b_{2g}(\pi), b_{1u}(\pi), \text{ and } e_g(\pi))$ to the antibonding orbitals $(IIb_{1g}(\sigma), IIb_{2u}(\sigma), \text{ and } IIIa_{1g}(\sigma))$ become allowed and the transitions from the $e_u(\pi)$ orbital are split. (The lower symmetry does not affect the assignment of charge transfer bands.) The effect on the spectrum would thus be broadening and/or splitting of the observed bands; this is in fact not observed. The decammine seems to act (at least in solution) as a complex with D_{4h} symmetry.

The lack of splitting of the observed $d \rightarrow d$ transitions is, however, open to another, perhaps more realistic, interpretation: that the two halves of the molecule are relatively independent of one another and the transitions observed as Bands I and II are the sum of the $e \rightarrow b_1$, and $e \rightarrow a_1$ transitions, respectively, on each cobalt atom (as explained above). The principle effect of the amido bridge would then seem to be the shortening of the Co-N_a bond, producing an <u>axially</u>-<u>compressed</u> tetragonal perturbation on the d-orbitals. It is not possible to generalize this effect (compression of the $Co-N_a$ bond), since structural data on other amido-bridged complexes are not available.

The Value of \underline{q} and the <u>SCCC</u> Treatment - The output value of the cobalt atom charge, q, in the decammine ion calculation was +1.24. This value would indicate that, if it were desirable to recycle the calculation to obtain self-consistency (the SCCC treatment), a higher value of q should be used. Figure 10 shows the variation of the cobalt orbital coulomb energies (H_{ij}) with \underline{q} , and the relationship of the H_{ii} 's to the ligand coulomb energies for the series of cobalt configurations $3d^{8.50-q}4s^{0.15}4p^{0.35}$. As can be seen, at higher values of \underline{q} , the 3d orbital coulomb energy (H(3d)) approaches and crosses the ligand coulomb energies (H(2p)), etc.). The values of H(3d) at higher values of q would not conform to the criterion of Gray and Ballhausen⁶⁶, that the coulomb energies should have the ordering 2σ (ligand) < nd (metal) < (n + 1)s(metal) < (n + 1)p(metal). Thus the calculations were not recycled to self-consistency, and the calculated energy levels are given only qualitative significance.

The meaning of the value of \underline{q} obtained in this and other investigations is far from clear. In no case has a charge value greater than +1 been found for any central metal ion, and in most cases the charge is found to be +0.6 or less (in a recent <u>MO</u> calculation for the hexamminecobalt(III) ion, Wirth¹³³ has obtained a charge of +0.07 for the cobalt atom:



Figure 10. Dependence of coulomb energies of the various orbitals on the charge (\underline{q}) of the cobalt atoms. The circles represent the coulomb energies at $\underline{q} = +0.25$ which were used for the <u>MO</u> calculations.

he assumed the NH₃ ligands to be uncharged). In discussing the q value (+0.30) of the cobalt atom in the hexamminecobalt(III) ion obtained from Yamatera's MO treatment⁹⁸, Ballhausen has stated¹²² that "whereas in the ionic model the cobalt ion carries a charge of three positive units of electricity, these are now smeared over the whole complex, and the metal atom is nearly neutral. This result is in accord with the charge-neutrality principle..." The low values of q obtained in Wolfsberg-Helmholz MO calculations would seem to indicate a high degree of covalency. But Fenske⁸⁴ has observed that "appreciable covalency is an automatic consequence of the ... method." Thus, for the present at least, the charge q must be regarded as a parameter having little physical significance. Coulomb energies derived in SCCC treatments by variation of q should probably be rejected unless they conform to the Gray-Ballhausen criterion⁶⁶.

The overlap integrals used in <u>MO</u> calculations might also be regarded as having little quantitative significance. The values obtained for overlap integrals are dependent on the wave functions used in the calculations: Wirth¹³³ has shown the variation in the values of hexamminecobalt(III) overlap integrals that result from the use of different wave functions. The inclusion of ligand-ligand overlap also has a significant effect on group overlap integral values¹³³. Overlap integrals must be regarded, then, as having at best qualitative significance and are a major obstacle to regarding

the MO theory as quantitatively significant.

Wirth has shown¹³³ that by the use of more accurate wave functions and other input parameters and the inclusion of ligand-ligand overlap, the Dq value of the hexamminecobalt(III) ion may be calculated to within 10% accuracy. In treating complicated ions of lower symmetry, however, Wirth states that other effects, such as electron repulsion and configuration interaction, need to be taken into account and that "it is doubtful that the central approximations of the extended Wolfsberg-Helmholz approach are accurate enough to support these elaborate superstructures."

Thus, the results of <u>MO</u> calculations using the Wolfsberg-Helmholz approach should be regarded as being only qualitatively significant. An almost bewildering variety of approximations have been used in the various transitionmetal complex <u>MO</u> treatments, yet the results are, for the most part, qualitatively consistent with each other and with the results of the crystal field theory. Assignments of $d \rightarrow d$ transitions from the results of <u>MO</u> calculations should be regarded as realistic only if they agree with crystal field treatments. It is only in the assignment of charge-transfer transitions that the <u>MO</u> theory clearly overrides crystal field theory, since <u>CFT</u> can not account for them.

<u>The Spectrum of the Chloroaquo Ion</u> - The two resolved bands in the chloroaquo ion spectrum (Table XIII, Figure 8) at 18,500 and 21,000 cm.⁻¹ may be assigned as the e \rightarrow b₁

transitions (see Figure 20) for the two now-different cobalt atoms. The $e \rightarrow a_1$ transitions are masked by the chargetransfer band at 33,900 cm.⁻¹. The equality of the intensities of these two bands (see Table XIII) lend a credence to assignment of the bands to the same transition on different cobalt atoms. These assignments also support the view expressed above: that the two halves of the molecule are relatively independent and can each be treated separately as tetragonal systems with axial compression.

The band at 14,160 cm.⁻¹ ($\epsilon = 57$, see Table XIII) is assigned as a singlet-triplet transition, in conformance with assignments in the mono-nuclear cobalt ammines^{92,101} (see Section IIIC). Thus the band is assigned as either the e \rightarrow b₁ or e \rightarrow a₁ transition in which the excited state is a triplet (³E).

The high intensity observed for this band is rather surprising: in $Co(NH_3)_5Cl^{2+}$ the corresponding band has a molar absorptivity of less than 1^{92} . However, the mononuclear iodo-and-bromopentammines also have high intensity singlettriplet bands (log ϵ 's of 1.48 and 0.67, respectively⁹²). Jørgensen has attributed the high intensities to a delocalization effect in which a part of the large spin-orbit coupling constants of the heavy halogens is added to the small cobalt(III) spin-orbit coupling constant¹³⁴. A similar effect may be operative in the chloroaquo ion. Hydrogen bonding between the bound aquo and chloro groups would provide a mechanism for delocalization and would result in a greater
effective spin-orbit coupling constant (a similar mechanism may be operative in the chloronitrato ion if an interaction between the chloro group and a nitrato oxygen is assumed).

It is difficult to choose between the $e \rightarrow b_1$, and $e \rightarrow a_1$ assignment for the singlet-triplet transition in the chloroaquo ion. Linhard and Wiegel⁹² have shown that the frequencies of the two singlet-triplet bands $({}^{1}A_{1} \rightarrow {}^{3}T_{1}$ and ${}^{1}A_{1} \rightarrow {}^{3}T_{2}$) in the halopentammines decrease with increasing halide ion size. It therefore seems reasonable to assign the observed transition as the higher energy $e \rightarrow a_1$ transi-On the basis of this assignment it would be predicted tion. that there would be a similar band at lower frequency corresponding to the $e \rightarrow b_1$ singlet-triplet transition. The assignment of the observed band to the e \rightarrow a₁ transition must be taken as uncertain, at least until the second band is characterized (it is, of course, possible that the second band lies at a higher frequency and is masked by the allowed transitions: the observed band would then be assigned as the $e \rightarrow b_1$ transition).

D. Infrared Spectra

Infrared Spectra in the NaCl Region - The infrared spectrum of the hexamminecobalt(III) ion in the NaCl region has been examined by many workers¹³⁵ and band assignments have been made^{106-109,135}. The spectrum of hexamminecobalt(III) chloride from 650-2000 cm.⁻¹ is shown in Figure 11 (dashed curve) and the data are given in Table XV.



| | C0(NH ₃ |) ₆ Cl ₃ | | [(NH ₃) | 5CONH2C | Co(NH ₃) |) ₅]Cl ₅ ·2H ₂ O |
|---|----------------------|---------------------------------|-----------------------------------|--------------------------------------|---------------------|----------------------|---|
| 834 | (s) | 2850 | (sh) | 720 | (w) | 1410 | (vw) |
| 1330 | (s) | 2950 | (sh) | 830 | (s) | 1623 | (s) |
| 1358 | (sh) | 3150 | (s) | 1150 | (vw) | 3150 | (sh) |
| 1380 | (sh) | 3250 | (s,sh) | 1305 | (m) | 3230 | (s) |
| 1625 | (s) | | | 1334 | (s) | 3430 | (sh) |
| | | | | 1378 | (w) | | |
| [(NH ₃) ₅ | CoNH ₂ Co | (NH ₃) ₅ |] (NO ₃) ₅ | [H ₂ O(NH ₃)] | CONH ₂ C | COCl(NH | H ₃) ₄]Cl ₄ °4H ₂ O |
| 712 | (w) | 1386 | (vs) | 825 | (m) | 1390 | (w) |
| 832 | (s) | 1628 | (s) | 855 | (sh) | 1410 | (w) |
| 1048 | (w) | 3170 | (sh) | 940 | (w) | 1634 | (s) |
| 1300 | (sh) | 3290 | (s) | 1108 | (w) | 3150 | (s) |
| 1365 | (sh) | | | 1300 | (m) | 3270 | (s) |
| | | | | 1330 | (s) | 3450 | (s,b,) |
| | | [H ₂ O(| NH_3 $_4CON$ | NH ₂ CoCl(NH | 3)4]Cl4 | b | |
| | | 8 | 24 (s) | 31 50 (s |) | | |
| | | 13 | 20 (s) | 32 10 (s | ,sh) | | |
| | | 16 | 20 (s) | | | | |
| ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~ | | | 1 | | | | |

Table XV. Infrared spectra of some bridged cobalt ammine complexes in the NaCl region (KBr pellets).

^aFrequencies in cm.⁻¹; intensities in parenthesis (vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, b = broad).

^bPrepared by dehydration of the hydrate <u>in vacuo</u> over P_2O_5 .

The bands in the NaCl region are due to vibrations of the ligand in the Co-NH₃ system (C_{3v} symmetry). The bands may be assigned as follows^{106,107,135}: the 834 cm.⁻¹ band is due to a <u>rocking</u> vibration (ρ_r), the 1330 cm.⁻¹ band is due to the <u>symmetric deformation</u> vibration (δ_s); the band at 1625 cm.⁻¹ is due to the <u>degenerate deformation</u> vibration (δ_d), the bands at 3150 and 3250 cm.⁻¹ are the symmetric and assymmetric N-H stretching vibrations (ν_s and ν_{as}). Diagrams of these vibrations have been given by Nakamoto¹³⁵.

There are, in addition, two shoulders (at 1358 and 1380 cm.⁻¹) on the symmetric deformation band and two shoulders (at about 2850 and 2950 cm.⁻¹) on the stretching bands. These shoulders might arise because of hydrogen-bonding between the $\rm NH_3$ ligands and the chloride anions, but have thus far resisted characterization.

The spectral data for the nitrate and chloride salts of the decammine ion are given in Table XV and the spectrum of the decammine chloride dihydrate is shown in Figure 11 (solid curve). The decammine nitrate shows bands characteristic of the free nitrate ion, which have been discussed by Nakamoto¹³⁶. The assignments of the nitrate ion vibrations are as follows: $v_1 = 1048 \text{ cm.}^{-1}$, $v_2 = 832 \text{ cm.}^{-1}$, $v_3 = 1386$ cm.⁻¹, and $v_4 = 712 \text{ cm.}^{-1}$. Since these nitrate bands mask some of the characteristic ammine vibrations (particularly ρ_r and δ_s), the ammine band positions were determined from the spectrum of the decammine chloride.

The spectrum of the decammine chloride dihydrate is

shown in Figure 11 and the data are given in Table XV. The bands at 830 cm.⁻¹ and 1623 cm.⁻¹ may be assigned as the ammine rocking $(\rho_{\underline{r}})$ and degenerate deformation $(\delta_{\underline{d}})$ vibrations, respectively; the bands in the region 3000-3500 cm.⁻¹ may be assigned as N-H stretching vibrations; the shoulder at about 3430 cm.⁻¹ is probably due to lattice water¹³⁷. In the region in which the symmetric deformation $(\delta_{\underline{s}})$ vibration is expected, however, three bands now appear (1305, 1334, and 1378 cm.⁻¹). The assignments for these three bands will be discussed in the next section.

The spectrum of the chloroaquo chloride tetrahydrate is shown in Figure 12, and the data are given in Table XV. The following assignments may be made; the band at 825 cm.⁻¹ is the ammine rocking vibration $(\underline{\rho_r})$ and the band at 1634 cm.⁻¹ is the ammine degenerate deformation vibration $(\underline{\delta_d})$; the two bands at 3150 and 3270 cm.⁻¹ are the N-H stretching vibrations. In addition the broad band at 3450 cm.⁻¹ is probably due to lattice water (O-H stretching vibrations); the shoulder at 855 cm.⁻¹ and the band at 940 cm.⁻¹ are probably due to the wagging and rocking vibrations of the coordinated aquo group¹³⁷. The assignments of the bands at 1108, 1300, and 1330 cm.⁻¹ will be discussed in the next section.

It is of interest to note that the spectrum of the anhydrous chloroaquo chloride (Table XV) (prepared by dehydration of the hydrate <u>in vacuo</u> over P_2O_5) is quite different. The bands due to coordinated and lattice water disappear



and the two bands at 1300 and 1330 cm.⁻¹ merge to form one band. In addition, the weak band at 1108 cm.⁻¹ apparently disappears. These changes are evidence of both removal of the lattice water and a probable structural change.

Far Infrared Spectrum (CsBr Region) of $\underline{\mu}$ -amido-decamminedicobalt(III) Nitrate - The far infrared spectrum of the decammine nitrate was determined in a Nujol mull. The data are reported in Table XVI. The six bands are designated $\underline{\nu_A}$ through $\underline{\nu_F}$ in order of decreasing energy; these designations are simply identification labels for use in the discussion of the spectrum and have no theoretical significance. The assignments of these bands will be discussed in the next section.

E. <u>Normal Coordinate Analysis Calculations: Results and</u> <u>Discussion</u>.

The normal coordinate analysis calculations were done with the aim of fitting the pattern of the observed spectra for amido-bridged cobalt ammine complexes. The calculations were done separately for the two infrared spectral regions (NaCl and CsBr).

(a) The ammine and amido vibrations were analyzed as follows: the pattern of the spectrum of the equatorial ammine system (which corresponds to the spectrum of the hexamminecobalt(III) ion) was fitted with a set of diagonal force constants. A set of force constants was derived from the equatorial

| Frequency cm. ⁻¹ | Relative Intensity ^a | Designation ^b |
|--------------------------------|------------------------------------|--------------------------|
| 543 | w | ν _A |
| 516 | w | vв |
| 463 | w | ν _C |
| 402 | m | ν _D |
| 334 | S | $^{ m V}{f E}$ |
| 317 | sh | $^{\vee}{ m F}$ |

Table XVI. Far infrared spectrum (CsBr region) of μ -amidodecamminedicobalt(III) ion (Nujol mull).

^as = strong, m = medium, w = weak, sh = shoulder.

^bThese are identification labels only and have no other significance.

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system constants for use in the axial system calculations by an approximate adjustment for the different Co-N distances. A set of force constants was also derived from the equatorial system constants for use in the amido-bridge system calculations. The calculated patterns for the three systems were then used in interpreting the observed infrared spectra in the NaCl region.

(b) The decammine ion skeletal vibrations were analyzed by obtaining a set of force constants for the Co-N stretching and N-Co-N bending vibrations of the hexamminecobalt(III) ion and adjusting these constants for the decammine ion calculations. The observed spectrum of the decammine ion was then interpreted on the basis of the calculated pattern.

The Cobalt-ammine and Amido-bridge Systems - The diagonal force constants derived for the equatorial cobalt-ammine system are shown in the second column of Table XVII. Angle bending force constants are adjusted to the same units (millidynes/Å) as the stretching force constants by division by the appropriate equilibrium bond lengths. The vibrational frequencies for the cobalt-ammine system calculated by use of the force constants in Table XVII are given in the third column of Table XIX. Comparison of the data given in Table XIX with the spectral data for $Co(NH_3)_6Cl_3$ (Table XV, Figure 11) show that the pattern is indeed reproduced (no attempt

| Force Constant ^b | Equatorial System | Axial System |
|---|-------------------|--------------|
| Fr | 5.70 | 5.70 |
| F_{α}/r_{H}^{2} | 0.53 | 0.53 |
| $\mathbf{F}_{\alpha}^{i}/\mathbf{r}_{H}\mathbf{r}_{CO}$ | 0.17 | 0.20 |

Table XVII. Force constants for the cobalt-ammine systems^a.

^aForce constants in units of millidynes/A.

^bDefined in equation (5B-18).

| | | | | ~ | | | . a |
|-------|--------|-------|--------------|---------------------|------|--------------|----------|
| Table | XVIII. | Force | constants | tor | the | amido-bridge | system . |
| 10010 | * | LOTCO | 001100001100 | x 0 x | 0110 | | 0,0000 |

| = | 5.70 | millidynes/A |
|---|-------------|--|
| = | 1.00 | н |
| = | 0.10 | н |
| = | 0.53 | II |
| = | 0.15 | |
| | = = = | = 5.70 $= 1.00$ $= 0.10$ $= 0.53$ $= 0.15$ |

^aForce constants are defined in equation (5B-19).

| Vibra- tional Mode and Symmetry Species ^b | Descrip- tion ^C | Equatorial Co-NH ₃ System(force constants from Table XVII) | From Equatorial Force Constants | From Distance- Adjusted Force Constants (Table XVII) |
|--|-------------------------------|--|--|---|
| S _{4a,b} (E) | vas | 3248 | 3248 | 3248 |
| S ₁ (A ₁) | $^{\vee}$ s | 3138 | 3138 | 3138 |
| S _{5a,b} (E) | δd | 1558 | 1554 | 1557 |
| $s_3 (A_1)$ | δ _s | 1437 | 1362 | 1391 |
| S _{6a,b} (E) | ρ _r | 758 | 700 | 758 |

Table XIX. Results of the normal coordinate analysis calculations for the cobalt-ammine systems.^a

^aFrequencies in cm.⁻¹.

^bAs defined in Table VIII.

 $\frac{c_{vas}}{\frac{as}{d}} = \text{assymmetric N-H stretch}; \quad \frac{v_s}{\frac{s}{s}} = \text{symmetric N-H stretch}; \\ \frac{\delta_d}{\frac{\rho_r}{d}} = \text{degenerate deformation}; \quad \frac{\delta_s}{\frac{s}{s}} = \text{symmetric deformation}; \\ \frac{\rho_r}{\frac{\rho_r}{d}} = \text{rocking.}$

was made to fit the actual frequencies since only diagonal force constants were used and hydrogen-bonding effects could not be taken into account).

Two calculations were then performed for the axial cobalt-ammine system. In the first, the force constants obtained for the equatorial cobalt-ammine system were used unchanged. The calculated frequencies are given in the fourth column of Table XIX. In the second calculation, the force constant for the H-N-Co bending coordinates (F $_{\alpha}^{\prime})$ was increased slightly (from 0.17 to 0.20) in order to adjust for the decreased Co-N distance. The new set of force constants is shown in the third column of Table XVII and the calculated frequencies are given in the fifth column of Table XIX. In the above equatorial and axial cobaltammine calculations, a value of 1.00 millidynes/A was used for the Co-N stretching force constant (obtained from the hexamminecobalt(III) ion calculations discussed below). Since the Co-N stretching vibration does not affect the ammine vibrations (because of the large frequency separation), the Co-N stretching frequency is not reported in Table XIX. Vibrations involving Co-N stretching will be discussed below in connection with the decammine ion skeletal vibrations.

Two calculations were performed for the amido-bridge system. The first was performed by use of the force constants in Table XVIII, but with the H-N-Co bending force constant (F") derived from the equatorial system (0.17 millidynes/Å). In the second calculation, the H-N-Co bending

force constant was decreased (from 0.17 to 0.15) to adjust for the greater Co-N distance (2.2 Å). The calculated frequencies for the two calculations are given in Table XX.

The value of the Co-N-Co bending force constant $(\underline{F}_{\underline{\alpha}})$ is only approximate. In a study of NH₂ deformation frequencies in polymeric HgNH₂Cl, Mizushima and Nakagawa¹³⁸ have used a larger value for the Hg-N-Hg bending force constant (0.100 millidynes/Å) than for the H-N-Hg bending force constant (0.089 millidynes/Å). In the case of the amido-bridge system, a <u>smaller</u> value was taken for the Co-N-Co bending force constant (0.10 relative to 0.15 millidynes/Å for the H-N-Co bending constant) since the bending would actually involve two bulky Co (NH₃)₅ groups instead of two Co atoms.

The observed bands in the spectrum of the decammine ion (Table XVII, Figure 11) may now be assigned on the basis of the results reported in Tables XIX and XX. The bands at 3150 and 3230 cm.⁻¹ in the decammine chloride spectrum may be assigned as the ammine symmetric and assymmetric N-H stretching frequencies, respectively. The data in Table XIX show that the calculated positions of these bands do not change for the closer axial ammine groups. The calculated positions for the amido group N-H stretching frequencies (3138 and 3248 cm.⁻¹) fall between the ammine stretching frequencies. Since the ratio NH₃:NH₂ is 10:1, the intensities of the NH₂ stretching vibrations would be expected to be small, so that they are undoubtedly masked by the NH₃ stretching bands.

| Vibr Moc Sym Sp | ational le and metry _b pecies | Description ^C | From Force Con- stants Derived from Equatorial Ammine System | From Distance- Adjusted Force Constants (Table XVIII) |
|--------------------------|---|--------------------------|---|--|
| ^S 1 | (A ₁) | v_{as} (N-H) | 3228 | 3227 |
| s ₈ | (B ₂) | ∨ _s (N-H) | 3192 | 3192 |
| ^S 3 | (A ₁) | NH ₂ bending | 1340 | 1335 |
| ^S 7 | (B ₁) | NH ₂ wagging | 1185 | 1115 |
| $^{s}5$ | $(A_2)^e$ | NH ₂ twisting | 1080 | 1014 |
| s ₉ | (B ₂) | NH ₂ rocking | 345 | 324 |
| s_2 | (A ₁) | v_{s} (Co-N) | 459 | 458 |
| s ₆ | (B ₁) | v_{as} (Co-N) | 276 | 276 |
| s ₄ | (A ₁) | Co-N-Co bendin | g 137 | 137 |

Table XX. Results of the normal coordinate analysis calculations for the amido-bridge system .

^aFrequencies in cm.⁻¹.

^bAs defined in Table IX. ^c $_{\underline{v}_{as}}$ = assymmetric stretch; $\underline{v}_{\underline{s}}$ = symmetric stretch. ^dForce constants are the same as given in Table XVIII except that $\underline{F}_{\alpha}'/\underline{r}_{H}\underline{r}_{CO}$ = 0.17 millidynes/A.

^eRaman-active only.

The band observed at 1623 cm.⁻¹ should be the combined degenerate deformation vibrations of the equatorial and axial ammine groups, since the calculations for this band (Table XIX) show that the different Co-N bond lengths do not affect the calculated frequencies significantly. The band at 830 cm.⁻¹ may be the combined rocking vibrations of the equatorial and axial ammine groups. The calculations (Table XIX) show that the position should not change if the distance-adjusted force constants (Table XVII, Column 3) are used: the distance-adjusted force constants are therefore the preferred values for the axial ammine group.

The three bands in the region $1300-1400 \text{ cm.}^{-1}$ may be assigned on the basis of the calculated data in Tables XIX and XX and of their relative intensities (see Figure 11). The two more intense bands at 1305 and 1334 cm.⁻¹ may be the symmetric deformation vibration of the axial and ammine groups, respectively. The third band at 1378 cm.⁻¹ may be the NH₂ bending vibration of the amido group, because of both its low intensity and the calculated data in Table XX. The calculated position for the NH₂ bending vibration (using the distance-adjusted force constants) is 1335 cm.⁻¹-lower than the ammine bands. However, the relative intensities might indicate that the higher frequency band is due to NH₂ bending vibration; therefore, the force constants in Table XVIII should be regarded as only approximate.

The results in Table XX show that the NH_2 wagging vibration should be found in the region 1100-1200 cm.⁻¹. Since no such band is seen in Figure 11, the spectrum of the

decammine chloride was determined by use of a highly concentrated KBr pellet. A very weak band was observed at 1150 cm.⁻¹. This band may be <u>tentatively</u> assigned as the NH_2 wagging vibration. The reason for the extremely low intensity is unclear if the assignment is correct. The chloroaquo ion also gives a weak band in the same region (1108 cm.⁻¹, see Table XV, and Figure 12) and may support the above assignment. The weak band at 1150 cm.⁻¹ might, however, have a different cause (such as overtones).

The concentrated KBr pellet also showed two other weak bands at 720 and 1410 cm.⁻¹. The origin of these bands is not clear and might be associated with hydrogen-bonding effects. Indeed, the band at 1378 cm.⁻¹, assigned as the NH₂ bending vibration, may also be due to hydrogen-bonding of the ammine groups. The bands at 1378 and 1410 cm.⁻¹ may be similar to the shoulders observed for the hexamminecobalt(III) ion at 1358 and 1380 cm.⁻¹ and may be attributed to the same (unknown) cause; the NH₂ bending vibration may be as weak as the wagging vibration (at 1150 cm.⁻¹) and therefore may be masked by the ammine $\delta_{\rm S}$ bands. Thus, although the bands at 1378 and 1150 cm.⁻¹ are assigned as the NH₂ bending and wagging vibrations, those assignments must remain tentative.

The other amido group vibrations indicated in Table XX were not observed. The NH₂ twisting vibration is not infrared active, and was therefore not observed. The NH₂ rocking and Co-N stretching vibrations would actually involve skeletal vibrations; therefore the calculated frequencies are

meaningless. The skeletal vibrations will be discussed below. The Co-N-Co bending vibration would be expected to lie below 200 cm.⁻¹; since the force constants are only approximate, the calculated frequency (137 cm.⁻¹) is also approximate. The spectrum of the decammine ion was not determined below 200 cm.⁻¹.

The spectrum of the chloroaquo chloride (Table XV and Figure 12) may be interpreted in a similar manner. The bands at 1300 and 1930 cm.⁻¹ may be the symmetric deformation vibration of the axial and equatorial ammine groups, respectively. The weak bands at 1390 and 1108 cm.⁻¹ may be tentatively assigned as the NH₂ bending and wagging vibrations. As in the decammine spectrum, the NH₂ bending and wagging assignments are only tentative because of the low intensities. The weak band at 1410 cm.⁻¹ is similar to the 1410 cm.⁻¹ band in the decammine spectrum and might also have its origin in hydrogen-bonding. The other bands (and shoulders) in the chloroaquo ion spectrum have been discussed in the preceding Section (VID).

The Skeletal Vibrations of the μ -amido-decamminedicobalt(III) <u>Ion</u> - The force constants used in the normal coordinate analysis calculations for the decammine ion skeletal vibrations were derived from an approximate set of force constants calculated for the hexamminecobalt(III) ion. The force constants for the hexamminecobalt(III) ion were determined to match the observed spectrum. There is, however, much

dispute in the literature over the far infrared spectrum of the hexamminecobalt(III) ion. Block¹⁰⁸ reported only a band at 490 cm.⁻¹, which he attributed to the assymmetric cobaltnitrogen stretching frequency. Blyholder and Ford⁴⁷ observed a weak band at 502 cm.⁻¹ and a strong band at 330 cm.⁻¹. Nakamoto¹¹⁰ reported bands at 500, 476, 448, and 327 cm.⁻¹, and assigned the first three bands to the Co-N stretching vibration (split by the crystal field) and the last band to the N-Co-N bending vibration. Shimanouchi and Nakagawa¹⁰⁹ observed a strong band at about 320 cm.⁻¹. In addition, they observed some very weak bands at higher frequencies (585 cm.⁻¹ for the bromide and iodide salts and 503 and 492 cm.⁻¹ for the bromide salt). Their assignments agree with those of Nakamoto¹¹⁰.

In spite of the conflicting reports, the hexamminecobalt(III) ion spectrum certainly has a weak band at about 500 cm.^{-1} and a strong band at $320-330 \text{ cm.}^{-1}$. In the present investigation, this pattern was matched in a normal coordinate analysis calculation by use of the following force constants:

$$F_r = 1.00 \text{ millidynes/A}$$

 $F_{\Omega}/r_N^2 = 0.48 \text{ millidynes/A}$ (6E-1)
 $F_{rr'} = 0.05 \text{ millidynes/A}$

where $\underline{F_r}$ is the Co-N stretching force constant, $\underline{F_\alpha}$ is the N-Co-N bending force constant and $\underline{F_{rr'}}$ is the bond stretching interaction constant (see equation (20), Section VB). The fundamental frequencies of the hexamminecobalt(III) ion calculated from these constants (equation (1)) are:

$$v_1 (A_{1g}) = 353 \text{ cm}.^{-1}$$

 $v_2 (E_g) = 308 "$
 $v_3 (T_{1u}) = 511 "$ (6E-1)
 $v_4 (T_{1u}) = 308 "$
 $v_5 (T_{2g}) = 438 "$
 $v_6 (T_{2u}) = 309 "$.

Diagrams of these vibrations have been given by Nakamoto¹³⁹. The two T_{1u} frequencies (511 and 308 cm.⁻¹) correspond to the two bands observed in the spectrum. The calculated pattern also agrees with the calculations of Shimanouchi and Nakagawa¹⁰⁹.

The force constants for the decammine ion calculation were derived from the hexammine**q**obalt(III) ion diagonal force constants (\underline{F}_r and \underline{F}_q) by an approximate adjustment for the different bond lengths. The values of the decammine ion force constants used in the calculation are given in Table XXI. The force constants have been defined in equation (5B-22).

The results of the calculation for the decammine ion skeletal vibrations are given in Table XXII. The calculated frequencies are given in the second column. Only the eight A_{2u} and E_u vibrations $(v_1 \text{ through } v_8)$ are infrared active: the A_{1g} , B_{1g} , B_{2g} , and E_g vibrations $(v_9 \text{ through} v_{19})$ are Raman active. The nature of each vibration is given in the third column as a linear combination of the

| Table XXI. | Force | constants | for t | the | skeletal | vibrațions | of |
|------------|----------------|------------|--------|------|-----------|-----------------------|----|
| | the <u>µ</u> - | amido-deca | ammine | edic | obalt(II) | [) ion [°] . | |

| Fer | = | 1.00 | millidynes/ A |
|---|---|------|-----------------|
| F _r a | = | 1.25 | |
| $\mathbf{F}_{\mathbf{r}}^{\mathbf{b}}$ | = | 0.85 | |
| F_{α}^{e}/r_{e}^{2} | = | 0.48 | н |
| $F_{\alpha}^{a}/r_{e}r_{a}$ | = | 0.53 | |
| $\mathbf{F}_{\alpha}^{\mathbf{b}}/\mathbf{r}_{\mathbf{e}}\mathbf{r}_{\mathbf{b}}$ | = | 0.45 | 11 |

^aForce constants are defined in equation (5B-22).

| Species ^b and Activity ^a | Calcula Frequence cm. ⁻¹ | ted cy, | Distribution of the Vibration Among the Symmetry Coordinates ^d ,e |
|--|---|-----------------|--|
| A _{2u} (IR) | 5 36 (v | 1 ⁾ | $0.59s_2 - 0.61s_3 - 0.53s_4$ |
| | 404 (v | 2) | $0.52s_2 + 0.80s_3 - 0.30s_4$ |
| | 338 (v | 3 ⁾ | $0.89s_2 - 0.09s_3 + 0.45s_4$ |
| | 316 (v | 4 ⁾ | s ₁ |
| E _u (IR) ^f | 544 (v | 5 ⁾ | $0.62s_{5a} + 0.10s_{5b} - 0.34s_{6a} + 0.25s_{6b}$ |
| | | | $-0.355_{7a} - 0.065_{8b} - 0.545_{8a} - 0.095_{8b}$ |
| | 497 (v | 6 ⁾ | $0.25s_{5a} - 0.01s_{5b} - 0.12s_{6a} + 0.12s_{6b}$ |
| | | | $-0.71s_{7a}^{+0.02s_{7b}^{+0.64s_{8a}^{-0.01s_{8b}^{-0.$ |
| | 3 55 (ν | 7 ⁾ | $0.63s_{5a}^{+0.22s}_{5b}^{-0.35s}_{6a}^{+0.17s}_{6b}$ |
| | | | $+0.535_{7a}+0.185_{7b}+0.295_{8a}+0.105_{8b}$ |
| | 312 (v | 8 ⁾ | $0.795_{5a} + 0.025_{5b} + 0.445_{6a} - 0.425_{6b}$ |
| | | | $-0.02S_{7a}^{+0.00S}_{7b}^{-0.01S}_{8a}^{-0.00S}_{8b}$ |
| A _{1g} (R) | 5 09 (v | 9 ⁾ | $0.73S_{10} - 0.26S_{11} - 0.64S_{12}$ |
| | 340 (v | 10 ⁾ | $-0.925_{10} - 0.055_{11} - 0.405_{12}$ |
| | 316 (v | 11 ⁾ | s ₉ |
| | 97 (v | 12 ⁾ | $0.12s_{10} + 0.98s_{11} - 0.18s_{12}$ |
| ^B 1g ^(R) | 316 (v | 13 ⁾ | ^S 13 |
| | 304 (v | 14 ⁾ | ^S 14 |
| ^B 2g ^(R) | 438 (v | 15 ⁾ | ^S 15 |

Table XXII. Results of the normal coordinate analysis calcu-.lations for the skeletal vibrations of the μ amido-decamminedicobalt(III) ion^a.

| Species ^b and Activity ^a | Calculated Frequency, cm. ⁻¹ | Distribution of the Vibration Among the Symmetry Coordinates ^{d,e} |
|--|---|--|
| E _g (R) ^f | 526 (v ₁₆) | $-0.665_{16a} - 0.055_{16b} + 0.345_{17a} - 0.295_{17b}$ |
| | | $^{+0.595}18a^{+0.055}18b^{+0.115}19a^{+0.015}19b$ |
| | 409 (v ₁₇) | $-0.50s_{16a} - 0.17s_{16b} + 0.31s_{17a} - 0.28s_{17b}$ |
| | | $-0.64s_{18a} - 0.22s_{18b} + 0.35s_{19a} + 0.12s_{19b}$ |
| | 313 (v ₁₈) | $0.785_{16a}^{+0.235}_{16b}^{+0.515}_{17a}^{-0.285}_{17b}$ |
| | | $-0.005_{18a} - 0.005_{18b} + 0.025_{19a} + 0.005_{19b}$ |
| | 214 (v ₁₉) | $0.285_{16a} - 0.245_{16b} - 0.025_{17a} + 0.275_{17b}$ |
| | | $+0.195_{18a} - 0.165_{18b} + 0.645_{19a} - 0.665_{19b}$ |
| ^B 1u ^(I) | 438 (v ₂₀) | ^S 20 |
| B _{2u} (I) | 316 (v ₂₁) | s ₂₁ |

| 304 (v ₂₂) S ₂₂ | |
|---|--|
| ^a The force constants in Table XXI were used. | |
| ^b For D _{4h} symmetry. | |
| ^C IR = infrared active; $R = Raman$ active; $I = inactive$. | |
| ^d The symmetry coordinates are defined in Table X. | |
| ^e The coefficients are the normalized elements of the \underline{L}^{-1} matrix (the inverse of the eigenvector matrix). | |
| ^f Only one linear combination is given for the degenerate $(E_u \text{ and } E_g)$ vibrations. | |

symmetry coordinates defined in Table X. The coefficients of the symmetry coordinates were obtained by normalizing the rows of the inverse of the eigen-vector matrix (i.e. the \underline{L}^{-1} matrix). Only one linear combination is given for each of the degenerate vibrations (the \underline{E}_u and \underline{E}_g vibrations): the other combination may be obtained simply by reversing the coefficients of each set of degenerate symmetry coordinates.

The molecular motions involved in the infrared active A_{2u} and E_u vibrations are shown schematically in Figure 13. The vectors in the diagrams indicate only the relative directions of the atomic motions, but not the relative magnitudes. The magnitude of the cobalt atom motions will of course be much smaller than ammine group motions. The corresponding symmetric A_{1g} and E_g motions may be obtained simply be reversing the directions of the vectors on one side of the molecule. The symmetric B_{1g} and B_{2g} motions may be easily obtained by inspection of the corresponding symmetry coordinates. Since only the infrared spectrum of the decammine ion was determined in this investigation, only the infrared active A_{2u} and E_u vibrations will be discussed.

The $\underline{\nu_1}$, $\underline{\nu_2}$, and $\underline{\nu_3}$ vibrations (A_{2u}) differ only in the direction of motion of the cobalt atoms and axial ammine groups relative to the motion of the equatorial ammine groups. In the $\underline{\nu_2}$ vibration, all the atoms move in the same direction while in $\underline{\nu_1}$ the cobalt atom motions are the opposite of the ammine group motions. In ν_3 , the axial ammine group



Figure 13. Schematic diagrams of the A_{2u} and E_{u} skeletal vibration of the μ -amido-decamminedicobalt(III) ion. Only one of each set of degenerate E_{u} motion is shown. The dark circles are cobalt atoms, the open circles are nitrogen atoms. motions are opposite the equatorial ammine motions – the cobalt atoms remain stationary. The $\frac{v_4}{4}$ vibration is a pure assymmetric stretch and involves no angle deformation.

The E_u vibrations $\frac{v_5}{5}$, $\frac{v_6}{6}$, and $\frac{v_7}{2}$ also differ only in the relative directions of the atomic motions. In $\frac{v_6}{2}$ all the atoms move in the same direction, in $\frac{v_5}{5}$ the cobalt atom motions oppose the ammine group motions and in $\frac{v_7}{2}$ the axial ammine group motions oppose the equatorial ammine and cobalt atom motions. The $\frac{v_8}{8}$ vibration involves only equatorial ammine group motions.

A comparison of the calculated frequencies of the A_{2u} and E_u vibrations from Table XXII with the observed spectrum (Table XVI) shows that the pattern of the observed spectrum has been reproduced in the calculations. The three high frequency bands $\frac{v_A}{A}$, $\frac{v_B}{B}$, and $\frac{v_C}{C}$ (see Table XXVI) should be the $\frac{v_5}{V_1}$, $\frac{v_1}{V_1}$, and $\frac{v_6}{V_6}$ vibrations (see Table XXII) respectively. The $\frac{v_D}{D}$ band (at 402 cm.⁻¹) may be the $\frac{v_2}{V_2}$ vibration. The observed band at 334 cm.⁻¹ ($\frac{v_E}{V_1}$) is very broad and includes the shoulder at 317 cm.⁻¹ ($\frac{v_F}{V_1}$). The $\frac{v_E}{V_2}$ band (including $\frac{v_F}{V_1}$) may then be the sum of the $\frac{v_3}{V_4}$, $\frac{v_4}{V_7}$, and $\frac{v_8}{V_8}$ vibrations.

Lowering the symmetry to C_{2v} (the bent structure determined by Vannerberg²⁰ and shown in Figure 1) would cause the D_{4h} vibrations A_{1g} , B_{1g} , B_{2g} , E_g and B_{2u} to become infrared active. The corresponding bands are not observed experimentally, so that the decammine ion apparently acts as a complex with D_{4h} symmetry in the far infrared region. This conclusion

is in accord with the results of the <u>MO</u> calculations and the electronic spectrum of the decammine ion.

The three internal coordinates that were neglected in the calculation - two linear valence angle bending coordinates (E_u) and a torsional (A_{1u}) coordinate - are of little consequence. The torsional coordinate (twisting of the two halves of the ion in opposite directions) is not infrared active in either D_{4h} or C_{2v} symmetry. The two linear valence angle bending coordinates actually correspond to the Co-N_b-Co bending vibration. This vibration has been discussed in connection with the amido-bridge system and is expected to lie below 200 cm.⁻¹.

It is significant that the pattern of the observed spectrum of the decammine ion could be reproduced by use of the force constants in Table XXI. The differences in the values of the different stretching and bending force constants reflect only the differences in the bond lengths. The three different cobalt-nitrogen bonds $(Co-N_e, Co-N_a, and Co-N_b)$ in the decammine ion are thus electronically very similar. This conclusion agrees with the results of the <u>MO</u> calculations which indicate that the three types of bonds are all essentially <u>o</u>-bonds and that π -bonding contributes very little to the Co-N_b bond stability. The Co-NH₂ bonds in amido-bridged cobalt complexes are electronically, and therefore chemically, similar to the simple Co-NH₃ bonds in mononuclear cobalt ammine complexes.

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